THE ANALYTICAL DISTILLATION
OF PETROLEUM

BY

W. F. RITTMAN AND **E. W. DEAN**

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First edition, October, 1916.

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CONTENTS.

TABLES.

ILLUSTRATIONS.

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By W. F. Rittman and E. W. Dean.

INTRODUCTION.

This report presents the results of an investigation conducted by the Bureau of Mines for the purpose of assisting in the establishment of a satisfactory standard method for the analytical distillation of petroleum, a problem of great importance to the petroleum industry. Experiments were performed for the purpose of studying the characteristics of methods typical of those in use; comparative studies were made of the efficiencies of the principal types of fractionation apparatus available to the petroleum chemist; and the characteristics of a type of apparatus that the results of the experiments seemed to indicate was best adapted to the purpose were investigated in detail. Also, some experiments were made to determine the effect of cracking as a factor in the analytical distillation of petroleum in still heads.

sity. The authors acknowledge the interest and unusual mechanical skill of these coworkers, whose assistance resulted in overcoming many difficulties incident to the investigation.

PURPOSE OF REPORT.

This report, as was stated in the introduction, describes in full the results of an investigation by the Bureau of Mines for the purpose of helping to establish a satisfactory standard method for the analytical distillation of petroleum. The results of part of the work have already been published by permission of the bureau in a technical journal.[a]

In the analysis of petroleum and its products one of the most valuable methods of examination is that of quantitative distillation. A knowledge of the boiling range of a crude oil is important, especially in view of the differences in commercial value of constituents boiling between the various limits of temperature. At the present time gasoline is the most desired petroleum product, and a knowledge of its content in any crude oil is necessary in determining the commercial value of the oil. Methods of distillation are also important in the examination of refined products, of which gasoline is the most striking illustration.

Gasoline is generally sold on the basis of its specific gravity, certain gravities being regarded as most desirable. Too light gasolines are not desirable on account of the disadvantages of handling and storing them. Heavier gasolines must be handled differently when used in internal-combustion engines. In actual fact the property of density is of importance only because it bears an approximate relation to the important property of gravity. To measure the specific gravity of a gasoline is easy, but to measure its volatility is difficult, and for this reason the present system of grading continues, although its inadequacy is becoming generally recognized. Specific gravity does not bear a constant relation to volatility of gasolines from different sources and it does not tell anything about the variations in volatility of a single product. A gasoline made up partly of constituents too light to be safe and partly of others too heavy to vaporize easily may be of an average specific gravity that approaches the mark considered most desirable by purchasers. Certain rough tests, such as the drying test, are sometimes useful in supplementing the determination of gravity, but the only satisfactory and accurate method is to make an analytical distillation. This is rarely done by users of gasoline, although the refiners generally keep a pretty close check on this important detail.

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[a] Rittman, W. F., and Dean, E. W., The analytical distillation of petroleum : Jour. Ind. and Eng. Chem., vol. 7, 1915, pp. 185–195, 754–760.

Volatility, as indicated by distillation range, is the most important property in determining the value of a product. Gasoline that is "too light," or too volatile, is dangerous in storage and transportation, and serious losses by evaporation may occur. Gasoline that is "too heavy," or not sufficiently volatile, does not vaporize easily when drawn into an engine cylinder and therefore is not properly burned.

Accurate data concerning the optimum range of volatility seem to be lacking, but it is nevertheless certain that volatility is the predominating property in determining the value of motor fuels. In view of its importance, it is obviously necessary to be able to determine it by means of the most satisfactory distillation methods that can be devised.

Unfortunately, however, distillation methods have never been satisfactorily standardized, and frequent complaints are heard to the effect that the reports of different chemists often fail to agree with each other and rarely agree with the results obtained in the refinery. The chief cause of the lack of standardization seems to be that the scientific data regarding the fractionation of complex mixtures are not properly coordinated. The separation of constituents from mixtures of simple composition has been studied in great detail, but no analogous data are available for such products as hydrocarbon oils and tars.

A study has been begun under the direction of the Bureau of Mines which, it is hoped, will ultimately aid in improving this state of affairs. At the request of the bureau some preliminary experiments were conducted by Profs. M. C. Whitaker and F. J. Metzger, of Columbia University. Such parts of their unpublished report as seem of importance to this discussion are given here.

No one method for the analysis of crude petroleum has been carefully investigated and adopted for general use as has been done in the case of so many of our analytical processes, and chemists are, therefore, at liberty to choose whichever method is the most convenient or available.

In order to establish the composition of these oils (samples of Oklahoma crude, submitted by the Bureau of Mines) we have analyzed and tested samples No. 1470 and No. 1464 by each of the four methods described in the most recent books treating on the subject of petroleum analysis. The methods we have used may be briefly summarized as follows:

1. *Engler method.*[a]—Distill 100 c. c. of the oil from a glass distilling flask of specified dimensions, collecting separately the fractions passing over between the following temperatures: Below 150° C., 150° to 200° C., 200° to 250° C., 250° to 300° C., above 300° C. When the temperature reaches the maximum for each fraction the source of heat is removed and the temperature allowed to fall 20° and then heated again to the maximum of the fraction. This process is repeated until no more distillate is obtained for that fraction. The

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[a] Allen, A. H., Commercial organic analysis, 4th ed., vol. 3, 1910, p. 48.

temperature is then brought up for the succeeding fraction and the same practice or running up to a maximum and dropping back 20° is continued until the fraction is complete. The final temperature is carried up to the point at which only coke is left in the flask.

2. *Ubbelohde method*.[a]—Distill 100 c. c. of the sample in a distilling flask of approximately the same dimensions as that used by Engler, but by a uniform and continuous application of heat, collecting the various fractions between the temperatures as specified by Engler..

3. *Regnault method*.[b]—Distill 100 c. c. of the sample from a metal retort, connected with a metal condenser, water cooled. The heat is applied uniformly and continuously, and the fractions collected as in the Ubbelohde method.

4. *Nawratil method*.[c]—Distill from a glass retort, uniformly and continuously heated, collecting the several fractions as already indicated. This method is used by many American chemists.

In order that our results might be comparable, one with another, we have adhered to the temperature range indicated in the first or Engler method for the separation of the various fractions in all distillations.

A series of tables were prepared, showing the individual results of the various distillations in the Columbia laboratory. Table 1, containing summary figures, shows all that is of interest in this connection.

TABLE 1.—*Comparison of results of four analytical methods of crude-oil distillation.*

[Work done under direction of Profs. M. C. Whitaker and F. J. Metzger, of Columbia University. Samples are Oklahoma crude petroleum.]

Sample and cut.	Percentage distilled by—			
	Engler method.	Ubbelohde method.	Regnault method.	Nawratil method.
Sample 1470.				
Cut below 150° C....................	9.5	5.2	3.7	2.8
Cut 150° to 300° C....................	32.7	32.3	34.8	34.0
Cut above 300° C....................	52.9	56.0	56.0	57.5
Sample 1464.				
Cut below 150° C....................	16.7	11.5	9.5	11.1
Cut 150° to 300° C....................	28.3	30.8	31.2	30.2
Cut above 300° C....................	50.5	53.5	53.5	52.5

A comparison of the results obtained shows a wide discrepancy in the amounts of the various products obtained by the several methods of analysis, and this difference is especially great in the case of the " naphtha " (cut below 150° C.). From sample 1464 about one and three-fourths times as much " naphtha " is obtained by the Engler method as by the Regnault method, whereas in sample 1470 the naphtha obtained by the Nawratil method is less than one-third that obtained by the Engler method. The variations shown in the analysis of the oils by the different methods are directly in accord with

[a] Allen, A. H., Op. cit., p. 50.

[b] Redwood, Boverton, A treatise on petroleum, 3d ed., vol. 2, 1913, p. 206.

[c] Allen, A. H., Loc. cit.

our previous experience, extending over a series of years. We do not consider any of the existing methods as dependable. It is doubtful if any of these methods will give results even approximating those obtained in practical distillation. We frequently encounter disputes between producer and refiner as to the proper evaluation of an oil, due to the differences in results obtained by different methods of analysis. We have frequently urged, and still urge, that the whole question of crude-oil analysis and method of evaluation be subjected to the most thorough investigation, with a view to establishing a standard method of analysis and report. Such a method would be promptly adopted by the chemists, as was the case in the standardized methods of coal analysis, with the result that the specifications may be drawn with fairness to producer and purchaser, and deliveries checked by both parties with reasonable accuracy.

The commercial value of the transactions in crude petroleum would justify the establishment of investigation into the methods of evaluation on a broad plan. The investigation should not be limited to a few laboratory comparisons of methods, but should be taken up with the producers, refiners, and chemists, with a view to correlating their problems and interests.

SCOPE OF INVESTIGATION.

The object of the investigation reported in this bulletin has been to obtain data concerning fundamental principles of petroleum distillation, in the hope that knowledge thus acquired may lead logically to the establishment of a standard method. No attempt has been made to evolve details of procedure or to prescribe an exact method of operation for the distillation of oils, but on the contrary work has been done to determine what latitude in details is possible without interference with uniformity of results. If an exact method is to be prescribed, it should come after correct general principles have been applied by a sufficient number of workers to minimize or eliminate the factor of personal preference. It has been impossible to avoid the description of details, but it has in every instance been recognized that these details are not essential and that the value of the work lies chiefly in the general principles established.

The experimental work herein described has been divided into three parts, as follows:

(1) A comparison of the degrees of fractionation attained by three general methods of distillation.

(2) A comparison of the degrees of fractionation attained by various types of apparatus of the general class proved most favorable by the work of division 1.

(3) A study of the details of operation and action of the particular type of apparatus indicated as most favorable by the experiments of division 2.

MECHANISM OF THE PROCESS OF DISTILLATION AND CLASSIFICA-
TION OF METHODS.

A thorough review of the various methods in use for the distilla-
tion of petroleum would be difficult to prepare, would hardly be
sufficiently interesting or instructive to be worth the space required,
and would not be absolutely comprehensive, as many of the methods
or modifications of methods are not published, or, if published, are not
available. Distillation methods may, however, be simply and satis-
factorily classified under three heads as regards the mechanism of
the process of distillation.

When any mixture is subjected to distillation the composition of
the vapor just as it leaves the liquid is controlled by the properties
of the liquid. The proportions of various constituents, their vapor
pressures, and the mutual relations of solubility of the vapors in
the liquids all play a part in determining the composition of the
mixture that is given off. In general, however, the vapor is richer
in the more volatile constituents than is the original liquid.

Nearly all processes of distillation involve partial condensation of
the vapors, so that all of the vapor escaping from the liquid does
not pass over into the condenser. The tendency toward condensa-
tion is greatest with the constituents of lesser volatility (higher boil-
ing point); and the loss of the mixture that liquifies and returns to
the retort of the distilling vessel causes a still further change in the
composition of the remaining vapor, again in the direction of en-
richment with more volatile constituents.

Still another factor of importance is the washing that occurs
when the returning condensate and the ascending vapors come in
contact. Here again the readjustment of conditions toward equi-
librium results in still further enrichment of the vapor in volatile
constituents. It appears, therefore, that all the effects of distillation
tend toward separation of the more volatile from the less volatile
constituents, the more volatile predominating in the distillate and
the less volatile in the residue. When a distillation is carried to
completion, the first fractions or cuts contain most of the more
volatile and the later most of the less volatile substances. It is a
fact, however, that the attainment of approximately complete sepa-
ration is difficult, even when the constituents differ widely in boiling
points and considerable condensation and washing occur.

In view of the above facts, methods of distillation may be simply
and satisfactorily classified according to the degree of condensa-
tion and washing to which the vapors are subjected. There are, of
course, no hard and fast lines of demarcation, but the following
three classes are adequate in grouping the various methods for the
distillation of petroleum: (1) Distillation methods involving a

minimum of separation (owing to condensation and washing) in the vapor phase. (2) those involving a moderate degree of separation, and (3) those involving a maximum degree of separation.

CHARACTERISTICS OF DIFFERENT TYPES OF DISTILLATION METHODS AS APPLIED TO THE ANALYSIS OF PETROLEUM.

METHODS OF MINIMUM SEPARATION.

Methods of minimum separation have, in the classification given, been made to include either those in which the vapor goes unchanged from the surface of the boiling liquid to the condenser, or those in which this result is approximately obtained. The apparatus of Allen and Jacobs[a] entirely eliminates condensation by supplying the necessary heat to the vapor space of the distilling vessel with an inclosing electric heater. The same end may be attained by means of other devices, though perhaps not as simply. The Allen-Jacobs method has been employed in the experimental work reported in this paper and will be discussed in detail in a later connection. Other methods attaining approximately a minimum of separation are those involving the use of retorts, and flasks with low outlets, particularly the type known as the Lunge tar flask. (See Pl. I, p. 54.)

These methods have advantages and disadvantages, varying in degree with the type of apparatus used. Their inherent characteristic, minimum separation, is in the nature of a disadvantage, so that they are commonly employed only when a rough separation is desired. In some cases the elimination of mechanical difficulties incident to the use of more efficient apparatus renders desirable the use of such methods. The retort is an antiquated type of apparatus and there seems to be little in its favor except that it has been largely used and that many distillation results are in terms of the degree of separation which it furnishes. The chief mechanical difficulty with the retort is that accurate temperature measurements when it is used are almost impossible, as its shape makes difficult the proper location of the thermometer bulb. The Lunge tar flask is a more modern device, of about the same degree of efficiency as the retort and is rather satisfactory, though difficult to fill and clean when viscous liquids are treated.

METHODS OF MODERATE SEPARATION.

Most of the methods in general use for the analytical distillation of petroleum are of the type that involves moderate separation. The methods of the first class, involving minimum separation, have been most largely employed for the distillation of coal-tar products, and

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[a] Allen, I. C., and Jacobs, W. A., Physical and chemical properties of the petroleums of the San Joaquin Valley of California: Bull. 19, Bureau of Mines, 1911, pp. 1–60.

have not been generally adopted by petroleum chemists except for the treatment of asphaltic oils.

Three of the most commonly employed methods of this second class are the Engler, the Engler-Ubbelohde, and the Regnault, described on pages 7 and 8. The Engler-Ubbelohde apparatus is the type most generally employed and has been used in slightly modified form in the experiments reported herein.

Methods of the moderate-separation type are largely used for the analysis of petroleum, a fact which constitutes one of their chief advantages. They seem to be favored because of ease and simplicity of operation and also because the necessary standard apparatus is generally available in the market.

The sources of disadvantage are rather numerous. Chief among these is the degree of separation attained, which, while far from the minimum, is even further from a maximum. The necessity of employing apparatus constructed to conform within a few per cent to standard dimensions is a disadvantage which is only in part obviated by the fact that such apparatus is purchasable. Also it is difficult to obtain uniform results in duplicate distillations, owing to the fact that the results in all open-flask distillations vary with slight changes in external conditions. Deviations from the standard rate of distillation and from the prescribed arrangement of apparatus are fruitful sources of error, as are also temperature changes induced by air currents in the room in which the distillation is conducted.

METHODS OF MAXIMUM SEPARATION.

In discussing methods of maximum separation it should first be made clear that the word "maximum" does not mean "absolute." The absolute limit of separation is difficult to attain under the most favorable conditions, and small-scale laboratory operations with complex mixtures of wide range of boiling point approach very nearly the limit of the most unfavorable conditions. There seems, however, to be a degree of separation that is difficult to exceed, and in a way this may be regarded as the maximum efficiency possible in the field of the analytical distillation of petroleum.

A complete list of the various sorts of apparatus used to obtain efficient fractionation would be almost as impossible to make as would a list of all the analytical methods employed in the testing of petroleum. Young[a] furnishes an excellent discussion of the mechanism and action of still heads. A more comprehensive and recent discussion may be found in the article of Golodetz,[b] which, unfortunately,

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[a] Young, Sydney, Fractional distillation, 1903, pp. 150–179.
[b] Golodetz, A., Ueber fraktionierte Destillation im Laboratorium and ueber neue Rektifizierapparate: Chem. Ind., Jahrg. 35, 1912, pp. 102–108, 141–145.

is not as readily available to American chemists. Several types of still heads are discussed in subsequent pages, but only general points relating to the problems of petroleum distillation are considered here.

The inherent advantage of methods of maximum separation is that they show more nearly than do the other classes what constituents the oil distilled actually contains. For instance, if some hydrocarbon is present which has an actual boiling point of, say, 110° C., this constituent will practically all distill within temperature limits of about 100° to 125° C., and not be included in large part in a fraction separated between 125° and 150° C. If a method of laboratory distillation attains a higher degree of efficiency than the refinery practice it is intended to check, it may be of great value in the indication it furnishes of possible improvement in the latter. For example, the tendency among progressive refiners to install fractionating towers is a striking proof that principles developed in the laboratory are beginning to be applied commercially; the various columns using a filling of tile or cobblestones are purely and simply Hempel, and most of the various types of baffle-plate towers closely resemble conventional laboratory still heads.

One of the chief advantages of methods of maximum separation is that they work to attain a limit which is fixed by the nature and properties of the oil treated and not by mechanical details of the apparatus and method of procedure used.

Many of the advantages of methods of maximum separation have long been recognized but were not thought sufficient to offset several apparent disadvantages. Perhaps the primary objection to the use of rectifying apparatus lies in the fact that it is in many cases complicated and difficult to adjust and operate; also many of the conventional still heads represent artistic work on the part of the glass blower and are consequently expensive and fragile.

The use of still heads has in many cases been condemned because the special purposes that some particular pieces of apparatus were designed to fulfill were not recognized. Many fractionating columns are so constructed that they will work within certain definite ranges of temperature. Such problems as the separation of alcohol from water and benzol from toluol are important as types which receive attention in the laboratory. Obviously apparatus designed to work with such bodies, having boiling points near 100° C., can not be expected to meet the needs of the petroleum chemist, who deals with exceedingly complex mixtures boiling over a wide range. Fractionation is obtained by a combination of two effects, condensation of vapor and washing of ascending vapor with the descending condensate. Of these effects condensation is the one least desirable in distilling petroleum, as a still head which produces proper condensation at a temperature of, say, 100° C., will obviously condense ex-

cessively at 250° C. It is therefore evident, as a fundamental consideration, that the types of still heads most favorable for the analysis of petroleum are those designed to obtain thorough contact of vapor and condensed liquid rather than large condensation.

An objection often raised to the use of still heads is that they cause cracking, which is due in part to superheating of the liquid running back into the still after condensing in the column, and in part to the high temperature necessary in the liquid phase to drive the vapor over. This objection does not seem well founded, however, as it can easily be shown that the " superheating " theory is erroneous, and experiment shows that the point at which most petroleum hydrocarbons begin to decompose even moderately is much higher than is commonly supposed. Statements are found to the effect that petroleum begins to decompose between 200° C. and 250° C. under atmospheric pressure; but the experiments performed in this investigation have demonstrated that three typical classes of American petroleums—Pennsylvania, California, and Oklahoma petroleum—do not start to crack until they are heated to temperatures of 325° C. or over. Another objection raised against the use of still heads is that they are variable in effect and will not, in the hands of different operators, give as uniform results as may be obtained by the methods of moderate separation. This objection also seems to be without just foundation of fact, as is demonstrated by experimentally obtained figures that are discussed in subsequent pages.

REQUIREMENTS FOR A METHOD FOR THE ANALYTICAL DISTILLATION OF PETROLEUM.

The requirements of a method for the analytical distillation of petroleum may be outlined as follows:

1. The results of a distillation must be such that the report will meet the needs of both the scientist and the oil technologist.

This requirement is fundamental and is perhaps the most difficult of all to fulfill on account of mechanical difficulties, the needs of the two classes not seeming always to be identical. The scientist desires to know what an oil contains in the way of constituents of various physical and chemical properties. The petroleum technologist wants information regarding yields of commercially valuable products and prefers a method that will, as nearly as possible, parallel results in the refinery. It appears, however, that the end sought by the scientist should be given most consideration, because from the results of an analysis conducted on the " absolute " basis the petroleum technologist can obtain the information he desires, provided he makes a proper interpretation. The methods of different refineries vary considerably both in efficiency and with regard to the products that are put out. On this account analytical results duplicating those obtained by the methods of one set of refineries

would be of little use to technologists interested in a different method of production. In any event it would be difficult in a laboratory distillation to duplicate the results of a large-scale commercial operation. On this account also it seems best to work toward the obtaining of results that have significance on some definite scientific basis. Such results will be of equal value to all refiners who understand the characteristics of their own working processes, and who will take the trouble to interpret intelligently the results of a standard analysis.

2. A standard method of distillation must minimize or, if possible, eliminate cracking. The purpose of a distillation is to ascertain what an oil consists of. The determination of what can be made from it by cracking is another and different problem and one that is not necessarily related to distillation.

3. A standard method of distillation must be satisfactory to the laboratory worker. The method should not be too tedious or time-consuming, nor require too great skill. Most of the routine analyses in all lines of commercial work are of necessity made by chemists who are not elaborately trained and the methods with which they work should as far as possible be simple and free from possibilities of error. Advantages of this sort are likewise desirable, although perhaps not as necessary, to chemists who are highly skilled in the technique of analysis. The apparatus employed in a standard method must be easily obtainable or else the method must not be dependent on details of construction of the apparatus involved.

TECHNIQUE OF PETROLEUM DISTILLATION.

TEMPERATURE MEASUREMENT.

The first and fundamental need in the distillation analysis of petroleum is accurate temperature measurement. Until rather recently the possibility of error in this direction was not recognized and little attention was given to this phase of the problem. The difficulties of satisfactorily measuring temperatures are now realized, and in the related field of tar distillation [a] much care is taken in specifying conditions and precautions.

Two general methods of temperature measurement are possible in petroleum distillation—one is the use of mercury thermometers, the other the use of thermoelectric elements. Thermoelectric devices avoid many of the difficulties incident to the use of mercury thermometers, but are nevertheless impracticable for technical petroleum work because the apparatus necessary is costly and must be used by highly skilled operators.

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[a] Church, S. R., Methods for testing coal tar and refined tars, oils, and pitches derived therefrom: Jour. Ind. and Eng. Chem., vol. 3, April, 1911, pp. 227–233 ; Sharples, P. P., Distillation of tar: Jour. Ind. and Eng. Chem., vol. 5, June, 1913, pp. 466–469.

SOURCES OF ERROR IN MERCURY THERMOMETERS.

It appears, therefore, that attention must be concentrated on the use of the mercury thermometer. The attainment of the necessary accuracy is not difficult and requires only the observance of a few simple precautions, the necessity of which is obvious when one considers the nature of the possible sources of error. Errors are in general due to any or all of the following causes: (1) Volatilization of mercury in the capillary of the thermometer; (2) shrinkage of the mercury in the exposed stem, due to the fact that it is not at the same temperature as the bulb; (3) incorrect calibration of instruments.

VOLATILIZATION OF MERCURY IN CAPILLARY OF THERMOMETER.

The first of these sources of error is of importance only at the higher temperatures, and then the error is not necessarily great unless the temperature is high and an attempt is made to hold it for a considerable period of time. The avoidance of this error is so simple, however, that there is little necessity of running risks in this line. Most high-grade thermometers for high-temperature work have the space above the mercury column filled with nitrogen under pressure, a detail of construction that reduces to a minimum the possibility of error through volatilization.

SHRINKAGE OF THE MERCURY.

The second source of error is one that can not be eliminated by any simple mechanical device or method of construction. Thermometers are almost universally calibrated for total immersion of both bulb and scale, this method being without question the only logical one for general purposes. In use, however, and particularly in distillation work the scale of the thermometer is rarely or never at the same temperature as the bulb. In distillation measurements that part which projects above the cork in the mouth of the flask is at a temperature only a little above atmospheric. The part between the outlet of the distilling flask and the cork is at still another temperature which is considerably higher than that of the atmosphere, though still much lower than that of the bulb, which is in a current of live vapor.

The error is due to the fact that cooling causes a shortening of the mercury column, with the result that the apparent temperature is always lower than the actual temperature. The so-called "stem correction" is calculated by the use of a rather simple formula,

and its application is not difficult unless especial accuracy is sought. The formula given by Young[a] is as follows:

$$c = 0.000143(T-t)n$$

in which c is the calculated correction, to be added to the scale reading, T is the temperature observed on the scale, and t is the average temperature of the exposed part of the stem, determined by the use of an auxiliary thermometer, preferably of the "thread" type. The figure 0.000143, which is an empirical one, is claimed to give more accurate results than the absolute difference between the coefficients of cubical expansion of mercury and glass, which varies between 0.00015 and 0.00017 per degree centigrade for the different varieties of glass used in thermometers.

The importance of the stem correction is small at lower temperatures, but above 200° C. it becomes considerable. Several researches[b] have been devoted to it and methods are outlined in the literature by which accurate calculations may be made. In the distillation of petroleum, however, this correction may be disregarded without serious error, provided the standard method used specifies that the thermometer be of such size and so placed that the stem correction is always the same. Also, it must be realized that temperature readings are not accurate on an absolute basis, and represent only a convenient basis of comparison. The magnitudes of the correction values may be realized from the figures given in Table 2. One of the lists was compiled from figures published by Schluter,[c] who calculated the corrections for the standard Engler apparatus according to the most approved methods. The other figures were obtained from Wiebe[d] and can be found also in Holde.[e] The corrections were determined by actual measurements with thermocouples. The figures do not, however, seem as correct as those of Schluter.

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[a] Young, Sydney, Fractional distillation, 1903, p. 12.
[b] Wiebe, H. F., Berucksichtigung der Fadenkorrection bei der Temperaturbestimmung in den Mineröl-Siedapparaten : Petroleum Ztschr., Jahrg. 7, September, 1912, pp. 1304–1306. Holde, D., The examination of hydrocarbon oils and of saponifiable fats and waxes, 1st English translation from 4th German edition, 1915, 483 pages, p. 27. Schluter, H., Über die Berechnung der Fadenberichtigung für geeichte Thermometer : Chem. Ztg., Jahrg. 39, March, 1915, pp. 187–188, 202–204.
[c] Schluter, H., Loc. cit.
[d] Wiebe, H. F., Loc. cit.
[e] Holde, D., Loc. cit.

TABLE 2.—*Corrections for cooling of the emergent stem of the thermometer in the distillation of petroleum in the standard Engler flask.*

[The corrections in list 1 are calculated according to the most approved methods and undoubtedly are more correct than those of list 2, which were obtained by measurements with thermocouples and do not seem to be as accurate.]

List 1.[a]		List 2.[b]		
Observed reading.	Correction.	Observed reading.	Correction.	Actual temperature.
°C.	°C.	°C.	°C.	°C.
----------	----------	59.2	0.8	60.0
79.2	0.8	78.4	1.6	80.0
99.0	1.0	97.7	2.3	100.0
118.5	1.5	116.9	3.1	120.0
137.9	2.1	136.1	3.9	140.0
157.2	2.8	155.1	4.9	160.0
176.4	3.6	174.1	5.9	180.0
195.4	4.6	192.8	7.2	200.0
214.3	5.7	211.3	8.7	220.0
233.1	6.9	229.7	10.3	240.0
251.8	8.2	247.8	12.2	260.0
270.3	9.7	265.9	14.1	280.0
288.8	11.2	283.7	16.3	300.0
----------	----------	301.2	18.8	320.0

[a] From Schluter, H., Loc. cit.
[b] From Wiebe, H. F., Loc. cit.; also in Holde, D., Op. cit., p. 27.

INCORRECT CALIBRATION.

The third source of error, incorrect calibration of thermometers, requires little discussion. The obvious remedy is to purchase better thermometers, or, if this is impracticable, to recalibrate those already in stock. Methods of calibration are outlined in various texts[a] of physics and physical chemistry.

As a result of experience acquired in the course of the experiments herein described it has seemed the most advantageous procedure to use an accurate nitrogen-filled thermometer, and a flask with only a short length of neck above the side tube. A 2-inch length has been provisionally adopted as most satisfactory. The advantages are twofold: First, it is possible to read the temperature from a low point on the scale, thus avoiding the difficulty of having part of the thermometer hid inside the cork; second, practically the whole stem is outside the flask and at a temperature which can be easily measured by the use of an auxiliary thermometer in case it is desired to keep check on the magnitude of the stem correction. When a considerable part of the scale is inside the flask, as in the Engler or Engler-Ubbelohde method, the cooling effect may be less but it is more subject to variation, and in any event is not easily measurable. By making the inclosed length of stem short enough the error due to cooling of this part is rendered so small that it

[a] Ostwald, W., and Luther, R., Physiko-chemische Messungen, 1910, p. 97. Kohlrausch, F., Lehrbuch der praktischen Physik, 1905, 10th ed., p. 157. Waidner, C. W., and Dickinson, H. C., Testing of thermometers: Bureau of Standards Bull., vol. 3, No. 4, 1907, pp. 674–728; Bureau of Standards Circular 8, 2d ed., 1911, 52 pp.

may be regarded as a variable and estimated as if it were the result of a temperature which is the average of that of the vapor and that of the atmosphere outside.

RATE OF DISTILLATION.

The second necessity in a standard method, after temperature measurement has been satisfactorily settled, is to eliminate variations due to mechanical and operative factors. Perhaps the first of these factors to merit discussion is rate of distillation. In methods of minimum fractionation this factor is of little influence provided an unreasonable rate is not attempted. The composition of the vapor entering the condenser is the same as when it leaves the liquid in the flask, and it is therefore controlled by the liquid and in no way by the factor of time. The only thing to be avoided is ebullition so violent that it causes an admixture of considerable quantities of unvolatilized spray with the vapor.

The methods of moderate separation are most strongly affected by the rate of distillation, as in passing from the surface of the liquid to the condenser the vapor does not approach a state of equilibrium. The cooling of the walls of the flask has considerable effect and if the rate of distillation is varied the proportional amount of condensation varies likewise. Directions for all methods of moderate separation specify a uniform and standard rate of distillation, a recommendation which has the soundest possible foundation.

With methods of efficient fractionation the rate of distillation has an upper but not a lower limit. In passing through the still head or fractionating column a certain quantity of vapor may be brought to approximate equilibrium with the descending vapor in a given unit of time. If less vapor passes in the unit of time the equilibrium is practically unchanged. If the limit capacity of the column is exceeded, however, equilibrium is not attained and the results of the distillation vary. It appears, therefore, that with methods of efficient fractionation it is possible to distill at any desired rate less than the limit fixed by the fractionating capacity of the still head.

The unit adopted in measuring the rate of distillation also deserves mention. The customary and convenient procedure is to count drops falling from the end of the condenser. It is not recommended that this practice be discontinued, but it should be realized that the size of a drop is an unreliable unit of measure for general use. The size varies with the shape of the condenser tip and also with the surface tension of the distillate. Likewise if the size of the charge distilled varies, a rate measured by so many drops or even so many cubic centimeters per minute becomes of no significance. It is evident that the rate should be in terms of the quantity distilled. Thus one may

specify 2 per cent per minute, and if the charge is 200 cubic centimeters and the oil falls at an average of 40 drops per cubic centimeter, one may for convenience in laboratory work make use of the measure of about 25 drops in 10 seconds. It must, however, be remembered that the same rate would not apply to a different oil or a different size of charge. Because of these complications in fixing the rate of distillation, the desirability of not having to fix this factor with accuracy is most evident.

ATMOSPHERIC CONDITIONS.

The results of distillations by all classes of methods are influenced by barometric pressure and this should always be recorded in order that corrections may be made for it in case of necessity.

A factor closely related to rate of distillation is the effect of the temperature of the air around the flask, particularly as this is varied by air currents. Here again there is a difference in effect on the results of distillations by the three general methods.

Minimum-separation methods generally require insulation of the distilling vessel and are, therefore, free from variation due to atmospheric temperature changes.

Results in methods of moderate separation are strongly affected, as the fractionation obtained in these methods is due almost entirely to condensation of vapor, and this condensation is considerably affected by the temperature of the air in contact with the flask and also by the rate at which heat is carried away. The neck of the flask generally has a small heat capacity and is therefore sensitive to changes in external conditions.

The results in methods of maximum separation are more affected than in methods of minimum separation, but much less so than in the open-flask methods. The degree of fractionation is only partly dependent upon condensation, as the washing of the vapor by descending liquid plays an important part. Likewise some types of apparatus use a still head of large heat capacity, which tends to make the column insensitive toward small and temporary temperature changes. It is, however, desirable to avoid temperature fluctuations and on that account work should be conducted in a room tolerably free from air currents, and if the method employed is one of moderate separation it is desirable, as an additional protection against air currents, to use screens or conduct the distillations in a hood.

SOURCE OF HEAT.

One of the chief mechanical factors in distillation is control of the source of heat. This is closely related to rate of distillation, and, if from a gas flame, is also related to the matter of air currents.

Methods of heating may be divided into two general classes, according as the heat is supplied by combustion or electrically.

HEATING WITH GAS.

Of the combustion methods it seems unnecessary to discuss any except those requiring the use of gas, because few laboratories lacking this convenience would attempt a distillation of petroleum. The first essential of the gas burner is that it shall be possible to regulate the flame accurately. This is more or less difficult to accomplish with either the ordinary cock used on gas lines or with a screw pinchcock attached to the rubber-hose connection of the burner. The burner should be equipped with a sensitive valve of some sort, preferably a screw needle valve. The ordinary Tirrell burner is equipped with this feature, and also with an air-regulating device that works with a screw. Several other types of stock laboratory burners have similar equipment, but the authors' experience with gas heating has dealt chiefly with the Tirrell.

The protection of the flask from breakage by local superheating has not been studied in detail by the authors, as the method first tried proved satisfactory. The flask was supported on a piece of stiff asbestos board in which a circular opening was cut to expose the proper proportion of bulb to the flame. This opening may be covered with wire gauze if desired, though this precaution is generally unnecessary. The use of a sand bath is not recommended, as it does not materially reduce the danger of breakage and has the undesirable feature of heating the room and the operator's face excessively. The important thing is not to let the flame play on the walls of the flask above the level of the liquid in it. The flame itself should be protected from drafts, which can be done by inclosing it with a metal or gauze shield.

ELECTRIC HEATERS.

Methods of electrical heating have the two disadvantages of electricity not being generally available and of the apparatus requiring a moderate amount of preliminary adjusting before it will operate with a minimum of attention. The advantages are so great, however, that the installation of this type of heating equipment is more than worth the trouble it takes if any considerable amount of distillation work is to be done. A full discussion of these advantages would be too long for this report and might overemphasize the importance of this phase of the problem. It may be stated, however, that a primary and absolute advantage is reduction in the danger of breakage and in the danger of fire. During the past eight years most of the distillations conducted in the petroleum laboratory of the Bureau

of Mines have been with electric heaters. In all these distillations there have been perhaps a dozen instances in which a flask broke while being heated and in none of these instances has there been a fire. The advantage of safety is by no means the only one. The source of heat is made independent of air currents in the room, can be regulated with great exactness, and by proper insulation can be made to give a maximum of the generated heat to the distilling vessel and a minimum to the surrounding atmosphere.

The mechanical details of electrical heaters for flasks do not seem to have been worked out with sufficient exactness to meet general needs, and this fact is recognized by the authors, although they have worked out a satisfactory heater for use in the Bureau of Mines petroleum laboratories. The heater described in the following is by no means perfect, and the apparatus may even be found entirely unsatisfactory in other laboratories. It is hoped, however, that the description will furnish a basis for modification and that ultimately there may be put on the market cheap and satisfactory electric heaters that can be purchased by any worker and used on any electric circuit. That such a condition does not exist is largely due to the fact that there is no demand for such heaters, as the advantages of their use are not recognized.

The essentials of an electric heater are as follows:

1. It should be low priced, or those parts subject to deterioration should be cheap and easily replaceable.

2. It should be as nearly " fool proof " as possible. Many types of apparatus that would serve excellently in the hands of skilled chemists would be worthless when used by the partly trained men employed to do routine testing. Electric heaters should, therefore, be mechanically strong and should not be subject to damage by overheating. The heating element should either be so constructed that it can not be overheated or else the circuit should be properly equipped with fuses.

3. For petroleum distillation the heater must have great latitude. It must be able to supply the small amount of heat needed to distill light naphthas and must also be able to supply sufficient heat to carry vapor temperatures up to 300° C. and above in a crude-oil distillation.

4. The heater must be efficient; that is, the heating element must be inclosed in an insulating case that will prevent the escape of heat in any direction except against the distilling vessel.

DESCRIPTION OF HEATERS USED IN BUREAU OF MINES PETROLEUM LABORATORY.

A description of the type of heater developed in the petroleum laboratory of the Bureau of Mines may be of value to others interested in electrical equipment of this sort. The bureau laboratory

is supplied with alternating and direct current of 220 volts potential. The heaters have been designed for this voltage and would, therefore, need modification if employed with the more usual 110-volt current.

The heater in use consists of a heating element made of about 30 feet of nickel-chromium wire bedded in alundum and inclosed in a metal insulating case filled with dry powdered kieselguhr (infusorial or diatomaceous earth) or shredded asbestos. The heating element is attached to the asbestos cover of the case and does not rest on the insulating material, this construction rendering it possible to keep the latter in a light, unpacked condition, when its efficiency is greatest. The asbestos cover is fastened tightly to the metal dish, thus avoiding troublesome spilling of the insulating material.

The construction of the heater is shown in figure 1, which represents diagrammatically a section of the assembled heater and the plan of the heating element. The nickel-chromium wire for absolute safety should be covered with asbestos insulation, although this, as has been indicated, is not essential. A single heater made of

PLAN

SECTION

FIGURE 1.—Electric heater used in Bureau of Mines petroleum laboratory.

bare wire has proved as durable as any made with insulated wire. Bare wire is cheaper and is more satisfactory to work with in constructing the heater. About 30 feet of No. 24 B. & S. gage wire, which has a resistance of about 1.6 ohms per foot, is wound on a mandrel one-eighth inch in diameter, the resulting helix being about 20 inches long when unstretched. The helix is placed spirally on a

wooden mold, turned on a lathe to be identical in shape and size with the flask used in the distillations. The wire is held in place with brads thrust through from the interior of the hollowed out mold.

The alundum is applied in the form of a thick paste and worked well in to fill the interstices between the turns of the coil. It is not necessary to get the alundum between the individual turns of wire in the helix as even with the bare wire the coating of oxide formed provides sufficient insulation to prevent short-circuiting. The cement is allowed to dry for at least 12 hours on the mold, after which the brads may be pulled out and the mass of alundum and wire removed from the wooden form. Removal is facilitated by thoroughly greasing the mold before attaching the wire. At this stage of its preparation the heating element is very fragile and must be handled with great care. It is then "smoothed up" with a thin paste of alundum cement. It often happens that a cracked or broken element may be patched at this stage and restored to usefulness. The element is next dried for several hours in an oven at a tempera- of from 100° to 150° C., after which it is fired in a muffle furnace for at least 15 minutes. The last detail of procedure is desirable, though not essential, as the firing can be accomplished with heat supplied by the element itself. If this is done the heating must be gradual, because if too much current is run through while moisture is held by the alundum the heater may short circuit and burn out.

The complete element is attached to a heavy asbestos board, cut in the shape of a gasket to fit both the element and the containing dish. Binding posts are placed on this board, and it is fastened tightly to the dish that contains the insulating material. Any good insulating mixture may be used for this purpose, but kieselguhr seems to be the most efficient of the materials adapted to the tempera- ture conditions in such work. A metal container of the shape indi- cated in figure 1 is best on account of convenience in setting it up on a ring stand or tripod, but an ordinary tin or agate dish of the right size will serve.

These heaters, containing about 30 feet of wire and having an internal resistance of about 50 ohms, work with current densities varying from 0.5 to 3.5 amperes, which is sufficient to attain the highest temperatures necessary in the distillation of petroleum and is about all the wire of the heater will carry safely. The heaters have been used with a water rheostat and an ammeter, as in figure 2, which shows the units of apparatus used and how they are connected. A properly designed wire resistance would undoubtedly have ad- vantages, as its use would eliminate the necessity of employing an ammeter and would save space..

CONDENSERS.

In the course of the work a type of condenser has been used that meets satisfactorily the needs of the petroleum analyst. In distilling a crude oil, volatile products come over at first, and to prevent their loss through evaporation more efficient cooling is necessary than is furnished by tap water, especially in warm weather.
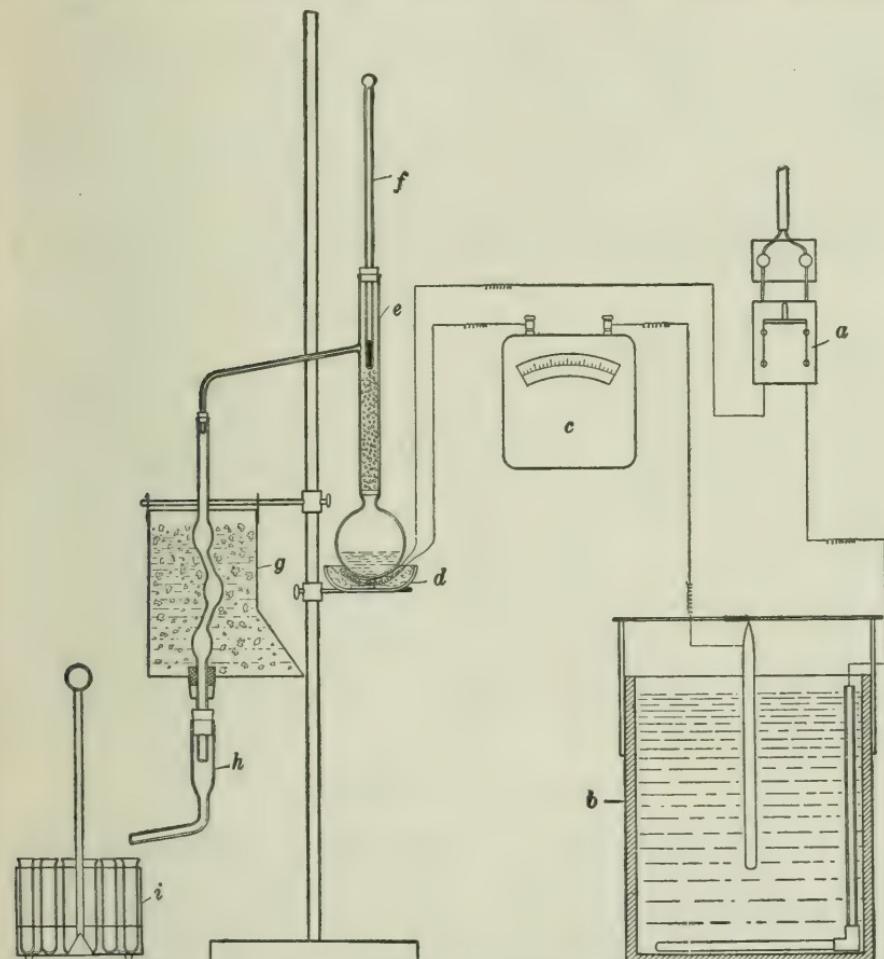
FIGURE 2.—Diagram of distillation apparatus assembled, with electric heater and water rheostat. *a,* switch at electric mains; *b,* water rheostat; *c,* ammeter; *d,* heater; *e,* distilling flask, with Hempel column; *f,* thermometer; *g,* condenser, with three-bulb tube and ice-filled jacket; *h,* adapter; *i,* metal rack containing receiving tubes packed in ice.

For the heavy lubricants driven over during a steam or vacuum distillation, and particularly when an oil contains paraffin, even an air condenser cools the vapors too much and there is trouble on account of lag or even clogging. The remedy is, of course, so to regulate the temperature of condensation as to reduce the viscosity of distillates and keep solid bodies in a molten condition.

In some earlier work in the bureau a vertical Leibig condenser was employed—a vertical position minimizes lag—and ice water was run through the jacket during the first stage of a distillation, while warm water was used during the period when viscous products were driven over. This procedure was later modified to attain the same end in a more convenient manner, by the elimination of running water as a cooling medium. A three-bulbed inner tube of glass is placed in an open-topped metal jacket. In condensing the lighter products the jacket is filled with ice or a mixture of ice and common salt, and for condensing the heavy viscous products it is filled with hot water, which is kept at any desired temperature by the application of heat from some external source. The condenser shown in figure 2 is one specially made for this purpose and has a projecting part that may be heated with a Bunsen burner. An admirable substitute for this piece of apparatus is one of the cylindrical cans commonly used as commercial containers for ether, alcohol, benzene, and the like. By cutting out the bottom of one of these cans and inverting it one may obtain readymade a jacket that possesses nearly all the desired qualities. The stopper that connects the inner glass tube should be wired in and care must be exercised when heating it not to burn this stopper. The shape of the bulbs and their staggered arrangement, shown in figure 2, are details of importance. The whole apparatus may be made with ease or can be obtained on special order from a chemical supply house, though it is not a stock article. A device of this sort has long been used in tar distillation, and is shown in catalogues of chemical supply houses, but the advantageous upright position of the condenser has not been adopted.

UNITS OF MEASUREMENT.

As commercial transactions in petroleum in this country are generally conducted on the basis of volume, it appears that the results of distillations should be reported in similar terms. In the petroleum laboratory of the Bureau of Mines, however, the more accurate system of measurement by weight has long been in use and has been continued in the experiments reported herein. Specific gravities have, however, been determined in all cases, which makes possible a transformation to terms of volume.

MEASUREMENT OF SPECIFIC GRAVITY.

The most convenient device for the measurement of specific gravity with small quantities of liquid is a balance of the Westphal or Mohr type. The ordinary Westphal balance is equipped with a plummet of 5 c. c. displacement. The 5 c. c. plummet serves well when 15 c. c.

of liquid is available, but for smaller quantities is useless, and a smaller one or a pycnometer must be used. By the method described by Weiss[a] it is possible to employ a small plummet on the regular Westphal balance and obtain results accurate to three decimal places. In some of the experiments this procedure has been adopted; in others a small balance with a plummet of 1 c. c. displacement has been used.

When the quantities to be measured are too small for even the special plummet, pycnometers are necessary; and a type has been employed which seems particularly adapted to the needs of the petroleum chemist. This type of instrument was devised by Prof. W. A. Drushel, of Yale University, for moderately accurate work with small quantities of liquids. His description is as yet unpublished. The description following relates to the needs of the petroleum chemist and does not cover the more general case.
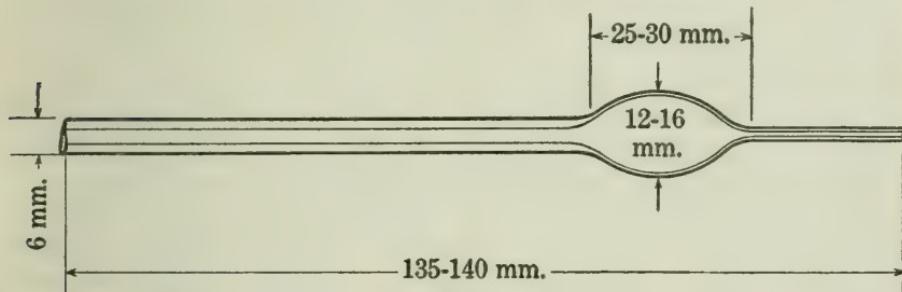
FIGURE 3.—Drushel pycnometer of dimensions and construction suitable for measuring specific gravities of petroleum distillates.

The Drushel pycnometer is simply a capillary pipette with a bulb of capacity between 1 and 2 c. c. and of dimensions approximating those indicated in figure 3.

In using the pycnometer the tube of oil is first brought to the desired temperature of 15° C. in a water bath. The calibrated pycnometer is then filled to the mark by suction, a bit of rubber tubing being used as a mouthpiece, after which the instrument is dried and weighed. From the weight obtained is subtracted that of the empty pycnometer. This result is then divided by the weight of pure water held by the pipette at a temperature of 15° C.

When one of these pycnometers is filled its contents are held so strongly in place by capillary force that there is little danger of displacement of liquid, provided a position approaching the horizontal is maintained. The more mobile naphthas must be handled with a little care, but even with them the difficulty is slight. The construction of the instrument may be varied to meet the needs of various sorts of oils. Thus, pycnometers may be made with tips of fine bore

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[a] Weiss, J. M., Specific gravity, its determination for tars, oils, and pitches: Jour. Ind. and Eng. Chem., vol. 7, January, 1915, pp. 21–24.

for the lighter naphthas and with heavier tips for viscous products. In any case, the surface for evaporation is negligibly small; hence, no protecting caps are necessary, though it is possible to use them without much additional difficulty. For work within a limit of error of 0.1 per cent, it is necessary to weigh only to milligrams; and a cheap balance may be used when one of the ordinary analytical type is not available. A horn-pan balance will serve the purpose if it is carefully handled.

EXPERIMENTS TO DETERMINE RELATIVE EFFICIENCY OF THE THREE GENERAL METHODS OF DISTILLATION.

Abundant and satisfactory data with regard to the effect of various methods of distillation on mixtures of two and three components are available,[a] but data concerning the degrees of fractionation attained with complex mixtures like petroleum are rather incomplete and not properly coordinated. It was necessary, therefore, to make careful preliminary determinations of the relative degrees of efficiency of the general methods when applied to the fractionation of petroleum.

As in such work it was impossible to start with a mixture of known composition, a simple method of procedure was devised that furnished a satisfactory index of the degree of separation attained.

The scheme of procedure was as follows: A single large sample of Pennsylvania crude oil was divided into a number of smaller parts or samples, each of which was kept in a carefully sealed, separate container. This precaution was adopted in order to make sure that the oil used was in all cases the same, the possibility of change through continued withdrawal from a single large container being thereby eliminated.

With these samples several series of duplicate distillations were conducted by specific methods representative of each of the three general classes. The Allen-Jacobs method was taken as typical of the class of minimum separation; the Ubbelohde represented the class of moderate separation, and a Hempel column was used to insure efficient fractionation, as representative of the third class. Cuts were made at intervals of 25° C., and the fractions obtained carefully saved. Separate containers were used for each 25° cut obtained by each method. For example, all the distillates obtained by the Ubbelohde method for the range of 100° to 125° were kept in one bottle, those from 125° to 150° in another, and so on for all the cuts obtained by this method and by the other two.

The fractions obtained from all these primary distillations were then subjected to redistillation in the apparatus of one of the methods, and 5° cuts were made. The boiling range of the distillate, as indicated by the percentage yield and specific gravity of these cuts,

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[a] Young, Sydney, Fractional distillation, 1903, pp. 159–179.

was a satisfactory index of the degree of fractionation attained in the primary distillation.

Most of the redistillations were conducted in the Hempel apparatus, which was the most efficient of the three. A subseries, however, was conducted of redistillations of Ubbelohde cuts in an Ubbelohde flask. The cuts from this redistillation were saved for 25° intervals and again redistilled in the Hempel apparatus. In this way it was possible to compare the degree of separation attained through two successive distillations by one of the methods of moderate efficiency with the degree attained by the use of a still head of the Hempel type.

DESCRIPTION OF SPECIFIC METHODS TESTED.

ALLEN AND JACOBS METHOD.

The method of Allen and Jacobs was developed for the treatment of petroleum such as California petroleums, which have an asphaltic base and are as a rule viscous, tarry liquids. They are particularly liable to hold water in an emulsified condition and often distill badly in the Engler flask. The method is particularly effective in obviating difficulties from water, as the inclosing heater prevents any condensation in the neck of the flask and renders impossible the near explosions that occur when drops of water fall back into the boiling oil. An example of the effectiveness of this method in distilling a difficult mixture is described in Bulletin 19.[a] The oil treated contained 33 per cent of water and 30 per cent of an asphaltum which was brittle at room temperature.

The fundamental idea in the development of this method was that no condensation should occur in the vapor space of the distilling flask. To attain this end a heater was used which was effective over the entire surface of the flask. A full description of the heater and the method of its construction is given.[b] A series of experiments, described in the bulletin, resulted in the adoption of a system of wiring that seemed to give the desired result—namely, uniform temperature throughout the entire distilling flask during the whole course of a distillation. It was later observed by A. S. Crossfield, then with the bureau, that the result could be only approximately attained by a fixed system of wiring. If the temperatures of the liquid and the vapor are equal at the beginning of a distillation, then the temperature of the vapor is lower at the end. The best attainable arrangement was one that gave equality at the middle point of the temperature range. A possible way of obtaining uniform temperature throughout the flask would be by uniform insulation of all its parts. So far, however, the method followed has been to vary the relative amounts of heat supplied to the bulb and the neck of the flask during

[a] Allen, I. C., and Jacobs, W. A., Physical and chemical properties of the petroleums of the San Joaquin Valley, Cal.: Bull. 19, Bureau of Mines, 1911, p. 19.

[b] Allen, I. C., and Jacobs, W. A., Loc. cit.

the course of the distillation by equipping the neck with an excess of wire and shunting a variable resistance across the top of the bulb, as shown in figure 4. By adjusting this resistance at intervals it is possible to maintain a proper ratio between the amounts of electrically generated heat supplied to the various parts of the distilling flask.

If the temperature in all parts of the flask is uniform, it is obvious that the position of the bulb of the thermometer or the hot junction of the thermocouple used in measuring temperature is of no consequence. It is obvious also that if the temperature of the vapor is higher than that of the liquid no condensation will occur, and the vapor must pass unchanged from the surface of the liquid
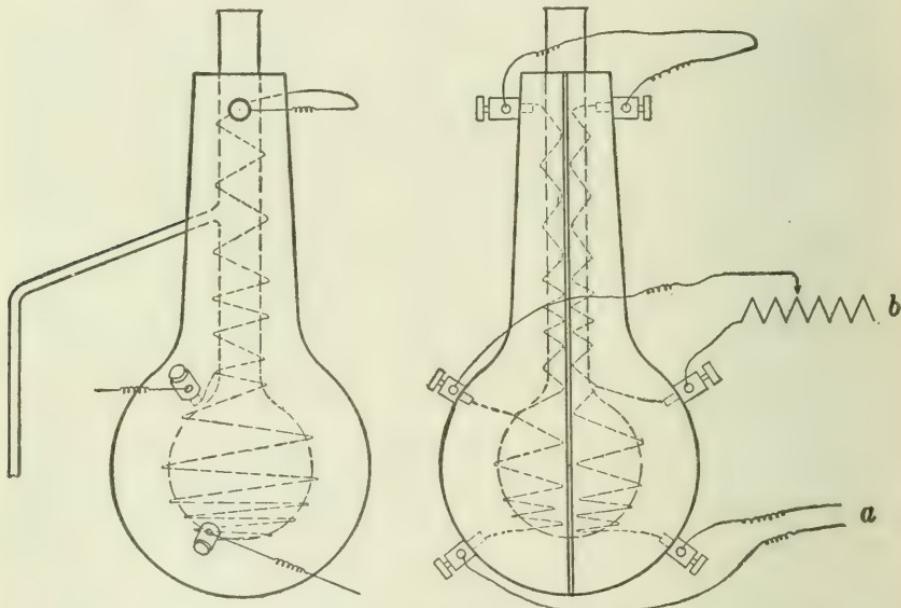
FIGURE 4.—Allen and Jacobs apparatus, modified to permit independent control of quantities of heat supplied to bulb and neck of distilling flask. *a*, wires connecting with electric mains; *b*, variable resistance shunted across top of bulb.

to the outlet of the flask. This, it will be remembered, is the essential condition of the method. It follows, therefore, that it is possible to make cuts on a basis of the temperature of the liquid as long as the vapor is slightly superheated. The superheating should not be excessive, in order that the possibility of cracking in the vapor phase may be eliminated. The mechanical difficulty of maintaining the temperature of the vapor within, for example, 20° of that of the liquid, is decidedly less than that of preserving equality of temperature.

In order to verify the above theoretical considerations, actual experiments were made with the two systems, the results of which are shown in Table 3, following.

TABLE 3.—*Comparison of results obtained by a modification of the Allen and Jacobs method, with results of the method as originally developed.*

Temperature, °C.	Percentage of distillate.		
	A.	B.	
150...........	3.8	3.5	Experiment A, vapor kept 6° to 26° hotter than the liquid.
175...........	7.3	7.1	Experiment B, temperatures of va-
200...........	7.6	7.7	por and liquid kept within 1° or 2°
225...........	7.3	7.5	of each other.
250...........	6.9	6.8	
275...........	6.5	6.7	
300...........	6.3	6.3	

ENGLER-UBBELOHDE METHOD.

The Engler-Ubbelohde method is so familiar to petroleum chemists that it needs little further discussion. Experience has indicated that with this method nice manipulation is necessary to insure moderately satisfactory agreement between the results of duplicate distillations. The difficulty seems to be due to the fact that the apparatus is extremely sensitive to slight variations in external conditions, as indicated in the discussion of the characteristics of the general classes of methods.

In the experiments reported herein the method was slightly modified in order to make the results comparable with those of the Hempel and inclosed-heater distillations. The upright c o n d e n s e r was used, 25° cuts were made, and the rate of distillation was s l o w e r than that generally prescribed. The flask used was of 250 c. c. capacity and of the dimensions shown in figure 5.
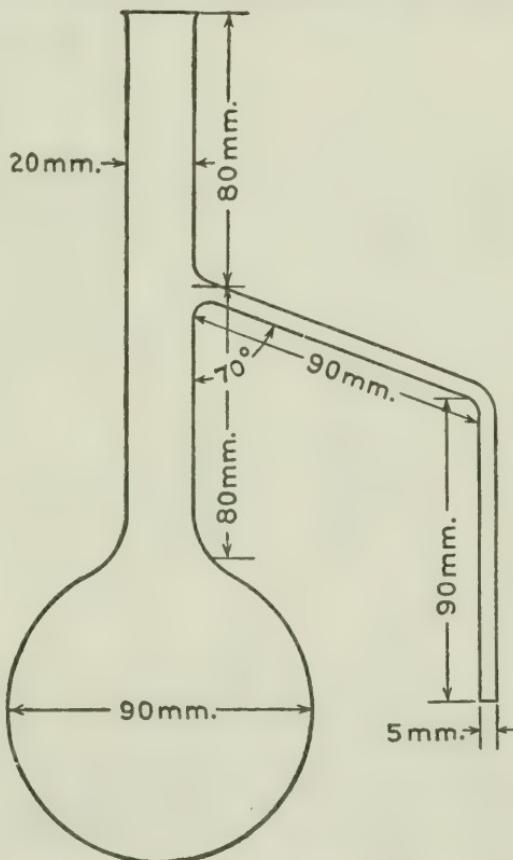
FIGURE 5.—Engler type flask of 250 c. c. capacity, used in Ubbelohde distillations.

HEMPEL METHODS.

For the primary series of distillations one of the standard creosote flasks (fig. 6) of the Forest Service, United States Department of Agriculture, was used.

These flasks have the fractionating column and bulb made in one piece, a detail of construction which obviates the difficulty of obtaining a tight joint between a short-necked bulb and an attached Hempel column. An additional advantage is that these flasks are standard articles which can be purchased from the regular stock of the chemical supply houses.

Aluminum beads were used in the fractionating column, as they seemed more satisfactory than glass. They were of the type used in the steel industry, being ellipsoidal in form and with the greater diameters between one-eighth and three-eighths inch.

In beginning a distillation the flask, with a spiral of iron gauze and the beads to be used, was counterpoised on a balance. The charge of oil was then weighed in and the fractionating column adjusted. The spiral of gauze, which had a wire attached, was inserted so as to rest on the

FIGURE 6.—Standard Hempel creosote flask.

constriction at the base of the neck. The beads were then poured in, the thermometer inserted, and connections made with the condenser. At the end of a distillation the cooled flask was weighed entire, and the difference between this weight and the original tare was a measure of the undistilled residue. To empty the flask the column of beads was loosened with a rod and removed by pulling on the wire attached to the spiral. The primary distillations for the Allen-Jacobs and the Ubbelohde series were made with original charges of 200 grams; for the Hempel primary distillations 300 grams were used.

PRIMARY DISTILLATIONS.

Although the results of greatest importance were those obtained from the redistillations, the figures resulting from the primary series are worthy of consideration, as they are in themselves a fairly definite index of the efficiency of separation attained.

RESULTS OF PRIMARY DISTILLATIONS.

The results of typical individual distillations and also the average of all the experiments of each series are shown in Tables 4 and 5. The important points are more clearly brought out by graphical than by numerical results and are discussed on pages 35 to 37 in connection with figures 7, 8, and 9. The numerical figures of most importance are those for the average variations, which indicate the ease with which concordant results may be obtained in duplicate distillations.

TABLE 4.—*Results of three series of primary distillations.*

[Each series represents a method typical of one of the three classes—minimum separation, moderate separation, and maximum separation.]

A.—HEMPEL METHOD (MAXIMUM CONDENSATION).

Temperature of cut, ° C.	Results of typical distillations.						Average of 13 distillations.	
	No. 1.		No. 2.		No. 3.			
	Percentage distilled.	Specific gravity.	Percentage distilled.	Specific gravity.	Percentage distilled.	Specific gravity.	Percentage distilled.	Specific gravity.
100	5.2	0.691	4.7	0.689	4.9	0.692	5.0	0.692
125	5.7	.729	5.9	.729	5.2	.728	5.6	.729
150	5.4	.745	5.7	.745	6.2	.745	5.9	.745
175	6.9	.759	7.0	.759	6.2	.758	6.6	.760
200	6.5	.771	6.2	.771	6.8	.770	6.5	.771
225	6.3	.782	6.7	.781	6.5	.781	6.6	.782
250	6.7	.793	6.9	.793	6.6	.792	6.7	.794
275	7.2	.805	6.5	.805	7.3	.805	6.7	.806

TABLE 4.—*Results of three series of primary distillations*—Continued.

B.—UBBELOHDE METHOD (MODERATE CONDENSATION).

Temperature of cut, °C.	Results of typical distillations.						Average of 25 distillations.	
	No. 1.		No. 2.		No. 3.			
	Percentage distilled.	Specific gravity.	Percentage distilled.	Specific gravity.	Percentage distilled.	Specific gravity.	Percentage distilled.	Specific gravity.
125	6.9	0.702	6.1	0.703	5.8	0.702	6.5	0.709
150	6.8	.734	6.4	.733	6.7	.733	6.7	.736
175	7.3	.753	7.2	.749	7.4	.752	6.9	.753
200	7.0	.773	7.0	.764	6.8	.767	6.5	.767
225	7.4	.779	7.2	.778	7.2	.778	6.9	.779
250	7.1	.793	7.8	.788	7.6	.790	6.9	.790
275	6.2	.804	7.6	.802	9.0	.804	6.7	.801
300	6.2	.812	7.2	.813	5.9	.816	6.8	.813

C.—ALLEN AND JACOBS METHOD (NO CONDENSATION).

Temperature of cut, °C.	Results of typical distillations.						Average of 13 distillations.	
	No. 1.		No. 2.		No. 3.			
	Percentage distilled.	Specific gravity.	Percentage distilled.	Specific gravity.	Percentage distilled.	Specific gravity.	Percentage distilled.	Specific gravity.
150	4.5	0.712	4.5	0.709	4.9	0.711	4.7	0.715
175	8.1	.729	7.8	.728	7.7	.730	7.6	.733
200	7.2	.748	7.2	.748	7.4	.748	7.3	.751
225	7.2	.757	6.9	.763	7.0	.763	7.1	.764
250	6.9	.768	6.7	.776	6.8	.777	6.7	.777
275	6.5	.787	6.4	.788	6.4	.787	6.4	.785
300	6.3	.798	6.3	.797	6.7	.796	6.3	.798
325	6.1	.810	6.4	.806	6.3	.808	6.5	.809

TABLE 5.—*Summary of results of primary distillations by three general methods.*

Condensation temperature, °C.	Average of results by method of—					
	Maximum condensation.		Moderate condensation.		Minimum condensation.	
	Per cent.	Specific gravity.	Per cent.	Specific gravity.	Per cent.	Specific gravity.
100	5.0	0.692	None.		None.	
100–125	5.5	.729	6.5	0.709	None.	
125–150	5.9	.745	6.7	.736	4.7	0.715
150–175	6.6	.760	6.9	.753	7.6	.733
175–200	6.5	.771	6.5	.767	7.3	.751
200–225	6.6	.782	6.9	.779	7.1	.764
225–250	6.7	.794	6.9	.790	6.7	.777
250–275	6.7	.806	6.7	.801	6.4	.785
275–300			6.8	.813	6.3	.798
300–325					6.5	.809

DISCUSSION OF RESULTS.

The average variations were calculated as follows: The percentages for cuts between the same temperature limits for each method were averaged and the variations on each side of this average figure summed up. This summation figure, divided by the number of dis-

tillations in the series, gives the average variation for the particular cut. The mean of the average variations for all the cuts gives a figure representative of the entire series. This figure is, of course, on the basis of the whole original charge of 100 per cent; hence its magnitude by no means represents properly the degree of variation. Consequently the average variation has been calculated on the basis of the average cut for each 25° interval, which, as the latter figure is about 6 per cent, increases the average variation about 16 times, making it really representative of the actual degree of error.

It will be noted that the average variation (2.6 per cent) for the Allen-Jacobs series is less than with the other two methods, owing to the insulation of the neck of the flask and the consequent negligible effect of air currents, variation in rate of heating, etc. The va-
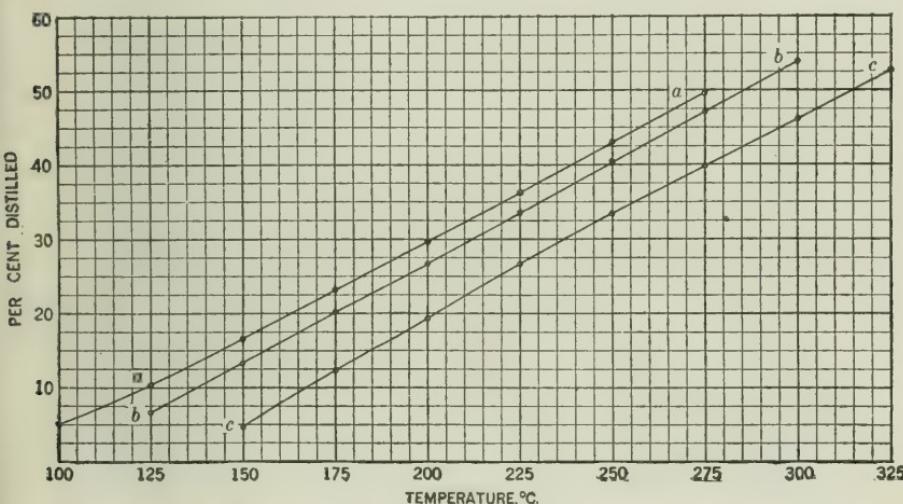
FIGURE 7.—Curves showing the relation of temperature and percentage distilled in primary fractionations by methods typical of the three general classes: *a*, Hempel; *b*, Ubbelohde; *c*, Allen and Jacobs. Note that the three curves appear to be nearly parallel and almost straight lines.

riation with the Ubbelohde method is, as would be expected, much greater and amounts to 6.3 per cent on the basis of the average 25° cut. The average variation (5 per cent) in the results of the Hempel series is less than that of the Ubbelohde series but greater than that of the Allen-Jacobs series.

It is to be noted also that with the Allen-Jacobs method the first cut was made at 150° C., with the Ubbelohde at 125° C., and with the Hempel at 100° C. Distillations were continued until the vapor temperature reached 325°, 300°, and 275° C., respectively, at which points approximately 50 per cent of the original oil had been distilled in each case.

A more general comparison of the results of the primary distillations may be made by the curves of figures 7, 8, and 9. Figures

7 and 8 show the relation between percentage distilled and temperature. In figure 7 the curves *a*, *b*, and *c* represent these relations for the average results of the Hempel, Ubbelohde, and Allen-Jacobs methods, respectively. On casual inspection these curves appear to be parallel straight lines, indicating that the results of the three methods are identical except as they differ with relation to the temperature scale. If this were the case it would be possible to consider the results of all distillation methods as equivalent and to use them simply by adding or subtracting a proper amount from the observed temperature. Figure 8, however, shows that the lines are neither
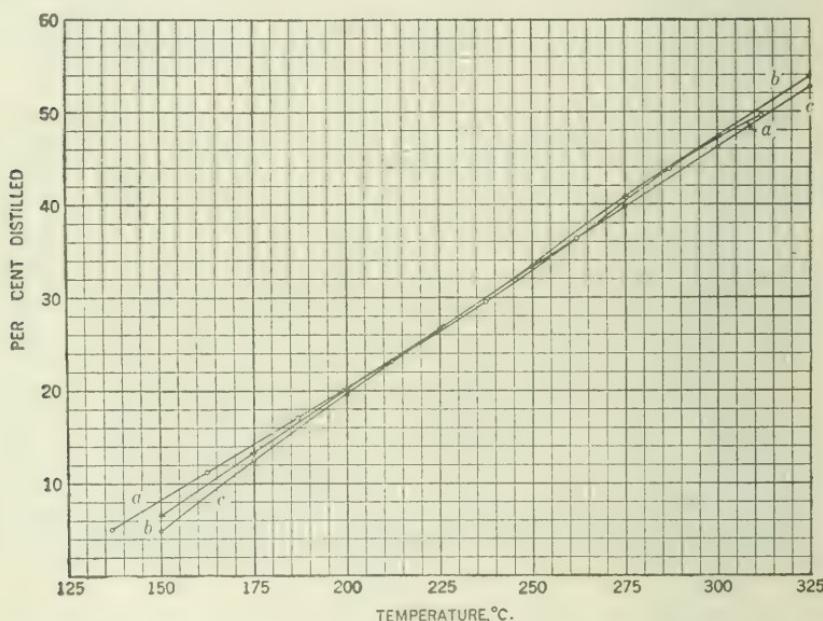
FIGURE 8.—Curves showing similarities and differences between temperature-percentage relations of primary fractionations: *a*, Hempel cuts with temperature limits 37° higher, and *b*, Ubbelohde cuts with temperature limits 25° higher than *a* and *b* in figure 7; *c*, Allen and Jacob cuts, limits same as *c*, figure 7. Note that the curves are actually neither parallel nor straight.

straight nor parallel. The curve *c* has the same temperature limits as curve *c* in figure 7; in curves *a* and *b* the upper limits are identical with those of *a* and *b* in figure 7, but the initial points have been moved away from the ordinate axis 37° and 25°, respectively. In figure 8 the curves *a* and *b* approximately coincide with *c* through a part of their course, but diverge at the lower end. As this is the part that represents the gasoline fraction the differences are of the greatest importance.

A study of the gravities of the cuts obtained by the different methods is particularly instructive. In figure 9 curves that represent approximately differential relations between specific gravity

and percentage distilled have been drawn by plotting the specific gravity of each cut against the average percentage distilled. It appears that, except in the first part of the curves, gravity percentage relations obtained by different methods are nearly the same. Again, however, it must be noted that the discrepancies occur in fractions which present commercial conditions have rendered most important.

These apparent similarities seem in a measure to explain the rather common but erroneous supposition that one method is about the same as another, provided a little care is used in the interpretation of results. Furthermore, in the past the lighter fractions were much less important than they are now, on which account
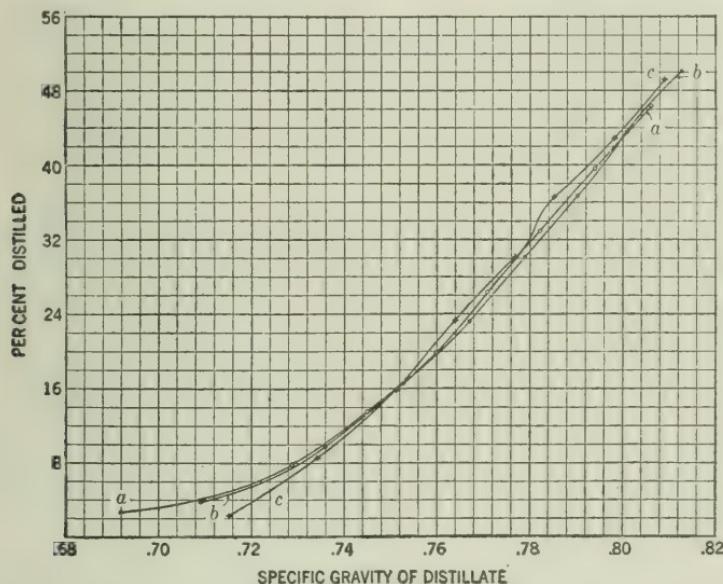
FIGURE 9.—Curves showing the relation of percentage and specific gravity in primary fractionations. Note differences at lower temperatures.

chemists have been more or less indifferent toward the variations that do occur.

These similarities were shown to be entirely superficial by the results of the redistillations, which indicated impressive differences among the degrees of separation attained by the three typical methods. The differences emphasize the danger of drawing conclusions on the assumption that there are more or less fixed relations among the results obtained with the different methods of analytical distillation.

REDISTILLATIONS.

Satisfactory qualitative information regarding the relative efficiency of various methods of distillation may be obtained by a study

of the results of primary fractionations shown in Table 4 and the curves representing them in figures 7 and 9. The characteristics of these curves have been discussed and it may be stated that the more efficient a method of distillation is, the closer the percentage-temperature curve is to the percentage axis. As regards the percentage-specific gravity relation, the curve for the more efficient method starts nearer the percentage axis, although through its main course it differs but little from that of the less efficient methods. Two simple devices for obtaining numerical indications of relative efficiency are (1) to note the temperature up to which some definite and moderately small percentage (3 to 6 per cent) distills, or else (2) to note the percentage distilling over up to some temperature not too high on the scale.

The methods of differentiation just indicated, while convenient, are not sufficiently accurate for the present work, and in fact conclusive evidence on which to base them was not obtained until the series of redistillation experiments, described in the following pages, were performed.

It is obvious that if in a distillation perfect separation is attained a fraction will, on redistillation, begin to boil at exactly the same original lower-temperature limit and will finish distilling at exactly the same upper-temperature limit. This ideal fractionation seems impossible to realize in petroleum distillation, even with the most elaborate fractionating apparatus; and the limit attained in the experiments, although it seems low, is probably somewhere near the possible maximum for apparatus of reasonably simple construction. It appears, however, that although at best only an approximate degree of separation can be obtained the use of a moderately efficient still head gives results much more nearly representative of the true composition of an oil than any of the methods of moderate separation. The percentage distilling between the original limits is about one and one-half times greater, and the amount distilling outside these limits is more nearly evenly divided between the fractions distilling above and below. With the methods involving a lower degree of separation, the percentage distilling below the original limits was between two and three times that distilling above. The figures obtained are approximately as follows: For the Hempel method the amount distilling below was 24 per cent, that above, 20 per cent; with the Ubbelohde method 48 per cent distilled below and 26 per cent above the original limits; with the Allen-Jacobs method the quantities were respectively 66 per cent and 20 per cent.

Redistillations were made with initial charges of 100 grams. The series of redistillation experiments may be summarized as follows: (1) Redistillations in Ubbelohde flask, of cuts from Ubbelohde pri-

mary distillations: (2) redistillations in a small-bulb Hempel flask,
of cuts obtained—(a) from Allen-Jacobs primary distillations; (b)
from Ubbelohde primary distillations; (c) from redistillations un-
der (1); (d) from distillations in Hempel flask.

RESULTS OF REDISTILLATIONS AND DISCUSSION OF RESULTS.

The only general feature to which attention need be called among
the redistillation data, given in Tables 6 and 7, is the matter of
regularity. The 5° cuts represent such small percentages in many
instances that they are of necessity subject to considerable error.
These individual errors tend to neutralize each other, however, and
a surprisingly good agreement will be noted among summation fig-
ures for the 25° intervals.

TABLE 6.—*Results of redistillations of 25° fractions obtained in primary series of distillations.*

[The results of the primary distillations are shown in Tables 4 and 5.]

SERIES 1.—REDISTILLATIONS OF ALLEN AND JACOBS CUTS IN HEMPEL FLASK.

Cut, 150–175° C.: specific gravity, 0.733.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
60	2.0	0.642
65	1.3	.662
70	1.6	.670
75	1.6	.680
80	2.2	.685
85	3.1	.693
90	3.2	.700
95	3.9	.707
100	5.4	.714
105	4.6	.718
110	6.4	.723
115	3.1	.728
120	5.2	.731
125	4.4	.733
130	4.2	.735
135	4.3	.739
140	3.8	.742
145	3.8	.746
150	3.1	.748
155	2.9	.751
160	2.8	.754
165	3.3	.757
170	2.4	.761
175	2.4	.763
180	1.6	.764
185	2.5	
Residuum		.782
Maximum 25° cut: Temperature limits, °C.	95–120	
Percentage redistilled.	24.7	
Percentage redistilled within limits of original cut.	14.1	

Cut, 175–200° C.: specific gravity, 0.750.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
85	3.4	0.683
90	3.4	.715
95	3.1	.716
100	2.9	.723
105	3.8	.725
110	5.2	.729
115	4.1	.733
120	4.6	.735
125	5.3	.737
130	4.7	.741
135	3.1	.747
140	4.4	.750
145	4.2	.752
150	4.7	.754
155	4.3	.757
160	3.8	.759
165	3.8	.761
170	3.3	.763
175	3.1	.765
180	2.9	.768
185	2.8	.770
190	2.7	.770
195	2.5	.773
200	2.1	.776
205	2.5	
210	2.0	
Residuum		.793
Maximum 25° cut: Temperature limits, °C.	125–150	
Percentage redistilled.	22.6	
Percentage redistilled within limits of original cut.	13.4	

Cut, 200–225° C.: specific gravity, 0.768.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
110	3.3	0.720
115	1.8	.730
120	3.1	.733
125	4.0	.736
130	2.8	.738
135	4.2	.742
140	2.8	.743
145	3.2	.747
150	3.9	.752
155	4.0	.753
160	4.2	.755
165	4.4	.757
170	4.4	.758
175	5.3	.763
180	3.8	.764
185	3.5	.765
190	4.2	.768
195	3.3	.772
200	3.3	.773
205	2.4	.777
210	2.8	.778
215	2.9	.779
220	2.2	.783
225	2.0	.784
230	2.4	.787
235	2.7	
Residuum		.806
Maximum 25° cut: Temperature limits, °C.	150–175	
Percentage redistilled.	21.7	
Percentage redistilled within limits of original cut.	13.2	

Cut, 225–250° C.: specific gravity, 0.777.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
135	4.9	0.739
140	1.5	.747
145	2.4	.748
150	2.3	.752
155	3.0	.755
160	3.0	.757
165	3.2	.759
170	3.1	.760
175	3.6	.763
180	2.8	.765
185	3.7	.767
190	3.8	.768
195	4.1	.769
200	3.2	.772
205	3.5	.773
210	3.6	.775
215	3.8	.777
220	3.8	.779
225	3.6	.783
230	3.5	.785
235	3.2	.787
240	2.9	.789
245	2.4	.790
250	2.3	.793
255	3.0	.795
260		.797
Residuum		.814
Maximum 25° cut: Temperature limits, °C.	170–195	
Percentage redistilled.	19.0	
Percentage redistilled within limits of original cut.	14.9	

Cut, 250–275° C.: specific gravity, 0.785.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
155	6.8	0.747
160	2.1	.757
165	2.7	.758
170	2.8	.762
175	2.5	.764
180	3.5	.766
185	3.7	.767
190	2.8	.768
195	3.3	.771
200	3.3	.772
205	3.8	.773
210	3.9	.775
215	3.4	.777
220	3.8	.777
225	3.4	.781
230	3.8	.781
235	4.1	.781
240	3.7	.784
245	3.9	.787
250	3.4	.788
255	3.4	.792
260	2.6	.793
265	2.2	.796
270	1.7	.798
275	2.9	.800
280		.802
285		.803
		.807
Residuum		.822
Maximum 25° cut: Temperature limits, °C.	205–230	
Percentage redistilled.	19.8	
Percentage redistilled within limits of original cut.	14.9	

Cut, 275–300° C.: specific gravity, 0.798.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
180	4.0	0.766
185	1.4	.772
190	1.5	.773
195	2.2	.774
200	2.5	.777
205	2.6	.778
210	3.4	.782
215	3.4	.782
220	2.9	.784
225	3.7	.786
230	4.1	.788
235	3.8	.789
240	3.3	.793
245	4.2	.795
250	3.2	.796
255	3.8	.799
260	2.7	.801
265	3.8	.803
270	3.8	.805
275	3.8	.807
280	2.3	.809
285	3.9	.810
290	1.6	.815
295	2.7	.814
300		.815
305		.818
310		
Residuum		.836
Maximum 25° cut: Temperature limits, °C.	235–260	
Percentage redistilled.	20.3	
Percentage redistilled within limits of original cut.	14.6	

Cut, 300–325° C.: specific gravity, 0.809.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
205	1.1	0.776
210	1.3	.781
215	2.0	.783
220	1.9	.784
225	2.1	.786
230	2.5	.788
235	3.1	.789
240	3.2	.792
245	3.2	.794
250	4.0	.796
255	4.1	.796
260	3.1	.800
265	4.2	.802
270	4.1	.803
275	4.2	.806
280	3.5	.807
285	3.8	.809
290	3.3	.810
295	4.5	.812
300	2.6	.814
305	3.0	.816
310	2.9	.817
315	3.0	.817
320	2.1	.821
325	2.3	.821
330	3.1	.823
335	15.2	.827
Residuum		.842
Maximum 25° cut: Temperature limits, °C.	250–275	
Percentage redistilled.	20.1	
Percentage redistilled within limits of original cut.	13.6	

SERIES 2.—REDISTILLATION OF UBBELOHDE CUTS IN HEMPEL FLASK.

Cut, 125–150° C.; specific gravity 0.736.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
85	3.8	0.679
90	2.5	.698
95	3.5	.707
100	3.1	.708
105	3.6	.718
110	2.9	.726
115	2.9	.729
120	2.0	.731
125	2.7	.732
130	2.4	.736
135	6.6	.738
140	4.7	.743
145	5.0	.747
150	3.9	.748
155	3.3	.749
160		

Residuum: 20.1

Maximum 25° cut:
Temperature limits, °C.: 105–130
Percentage redistilled: 34.5
Percentage redistilled within limits of original cut: 25.8

Cut, 150–175° C.; specific gravity 0.753.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
110	5.3	0.723
115	5.8	.732
120	4.9	.734
125	4.4	.737
130	4.5	.740
135	4.6	.742
140	5.6	.744
145	4.9	.748
150	7.2	.750
155	6.1	.753
160	5.1	.753
165	7.6	.757
170	4.6	.759
175	4.8	.763
180	2.8	.764
185	2.9	.765

Residuum: 16.8

Maximum 25° cut:
Temperature limits, °C.: 140–165
Percentage redistilled: 29.3
Percentage redistilled within limits of original cut: 26.2

Cut, 175–200° C.; specific gravity 0.767.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
135	3.3	0.712
140	6.8	.747
145	3.4	.749
150	4.5	.753
155	6.5	.753
160	5.7	.757
165	7.9	.759
170	7.2	.761
175	6.8	.763
180	5.5	.765
185	6.5	.767
190	4.5	.767
195	4.3	.768
200	3.3	.771
205	3.6	.775
210	2.7	.777

Residuum: .793

Maximum 25° cut:
Temperature limits, °C.: 150–175
Percentage redistilled: 34.1
Percentage redistilled within limits of original cut: 23.8

Cut, 200–225° C.; specific gravity 0.779.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
160	3.8	0.758
165	4.1	.762
170	4.1	.763
175	4.6	.766
180	6.3	.767
185	7.0	.768
190	6.3	.769
195	6.4	.771
200	5.2	.773
205	6.0	.774
210	4.9	.776
215	6.1	.778
220	4.9	.781
225	4.5	.782
230	3.6	.784
235	3.4	.787

Residuum: .800

Maximum 25° cut:
Temperature limits, °C.: 175–200
Percentage redistilled: 31.2
Percentage redistilled within limits of original cut: 24.4

Cut, 225–250° C.; specific gravity 0.796.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
185	4.8	0.771
190	2.1	.773
195	5.8	.775
200	5.6	.777
205	6.2	.778
210	5.7	.779
215	5.2	.781
220	7.6	.782
225	6.3	.785
230	5.4	.787
235	5.7	.788
240	4.7	.792
245	4.0	.793
250	3.5	.795
255	3.2	.797
260		.801

Residuum: .810

Maximum 25° cut:
Temperature limits, °C.: 205–230
Percentage redistilled: 31.0
Percentage redistilled within limits of original cut: 24.1

Cut, 250–275° C.; specific gravity 0.801.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
210	2.4	0.778
215	1.3	.786
220	2.3	.786
225	6.2	.787
230	6.3	.789
235	5.9	.792
240	6.6	.793
245	7.6	.795
250	8.5	.797
255	6.6	.799
260	5.2	.802
265	5.7	.802
270	4.4	.804
275	3.8	.807
280	3.4	.811
285	3.1	

Residuum: .822

Maximum 25° cut:
Temperature limits, °C.: 225–250
Percentage redistilled: 33.3
Percentage redistilled within limits of original cut: 23.7

Cut, 275–300° C.; specific gravity 0.813.

Temperature, °C.	Percentage redistilled.	Specific gravity of redistillation cut.
240	6.1	0.794
245	4.2	.794
250	4.9	.795
255	5.1	.796
260	6.0	.802
265	5.7	.805
270	6.3	.806
275	6.4	.807
280	5.4	.807
285	5.6	.809
290	5.1	.811
295	4.3	.812
300	4.0	.813
305	4.9	.816
310		

Residuum: .827

Maximum 25° cut:
Temperature limits, °C.: 255–280
Percentage redistilled: 28.8
Percentage redistilled within limits of original cut: 24.2

TABLE 6.—*Results of redistillations of 25° fractions obtained in primary series of distillations*—Continued.

SERIES 3.—REDISTILLATION OF UBBELOHDE CUTS IN UBBELOHDE FLASK.[a]

[Results not comparable with any of other series.]

Cut, 125–150° C.; specific gravity, 0.736.

Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.
95	1.9	0.702
100	4.0	.706
105	7.6	.716
110	13.1	.719
115	8.1	.724
120	7.7	.730
125	9.4	.734
130	7.5	.736
135	6.8	.738
140	3.6	.741
145	4.0	.746
150	4.2	.747
155	3.2	.751
160	3.0	.753
Residuum	14.6	.764

Maximum 25° cut: Temperature limits, °C., 100–125; Percentage distilled over, 45.9; Percentage distilled over within limits of original cut, 26.8.

Cut, 150–175° C.; specific gravity, 0.753.

Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.
120	1.7	0.729
125	4.0	.733
130	9.1	.738
135	13.6	.741
140	7.5	.744
145	8.0	.746
150	8.2	.748
155	6.5	.749
160	6.4	.753
165	6.3	.756
170	3.9	.758
175	4.0	.760
180	3.4	.762
185	2.7	.765
Residuum	14.1	.776

Maximum 25° cut: Temperature limits, °C., 125–150; Percentage distilled over, 46.4; Percentage distilled over within limits of original cut, 27.1.

Cut, 175–200° C.; specific gravity, 0.767.

Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.
145	1.2	0.747
150	2.5	.750
155	7.6	.754
160	10.4	.756
165	7.9	.758
170	9.6	.760
175	11.6	.762
180	7.9	.764
185	6.9	.765
190	5.5	.767
195	4.4	.768
200	3.8	.771
205	2.9	.772
210	3.3	.775
Residuum	15.0	.786

Maximum 25° cut: Temperature limits, °C., 150–175; Percentage distilled over, 47.3; Percentage distilled over within limits of original cut, 27.4.

Cut, 200–225° C.; specific gravity, 0.779.

Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.
170	2.5	0.763
175	2.2	.764
180	6.5	.765
185	11.2	.768
190	9.9	.770
195	9.2	.771
200	7.7	.772
205	7.2	.774
210	6.2	.775
215	5.7	.776
220	4.1	.782
225	4.0	.783
230	3.3	.784
235	3.0	.788
Residuum	16.6	.802

Maximum 25° cut: Temperature limits, °C., 180–205; Percentage distilled over, 45.7; Percentage distilled over within limits of original cut, 27.7.

Cut, 225–250° C.; specific gravity, 0.790.

Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.
200	3.4	0.773
205	4.1	.776
210	13.1	.778
215	9.8	.782
220	8.4	.783
225	9.1	.785
230	7.4	.787
235	5.7	.788
240	5.3	.790
245	5.2	.791
250	4.1	.793
255	6.4	.797
260	6.4	.797
Residuum	17.6	.808

Maximum 25° cut: Temperature limits, °C., 205–230; Percentage distilled over, 47.8; Percentage distilled over within limits of original cut, 27.7.

Cut, 250–275° C.; specific gravity, 0.801.

Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.
220	1.2	0.783
225	2.9	.787
230	5.6	.788
235	8.3	.790
240	12.2	.791
245	10.2	.794
250	8.4	.796
255	7.2	.797
260	5.3	.800
265	5.5	.802
270	4.8	.803
275	3.7	.806
280	3.2	.806
285	2.5	.808
Residuum	18.8	.819

Maximum 25° cut: Temperature limits, °C., 230–255; Percentage distilled over, 46.3; Percentage distilled over within limits of original cut, 26.5.

Cut, 275–300° C.; specific gravity, 0.81-.

Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.
245	3.4	0.787
250	1.5	.790
255	7.0	.792
260	5.4	.793
265	4.3	.795
270	8.8	.795
275	8.6	.797
280	7.1	.809
285	6.3	.809
290	4.0	.812
295	5.3	.814
300	3.9	.815
305	3.5	.816
310	3.0	.818
Residuum	20.5	.836

Maximum 25° cut: Temperature limits, °C., 260–285; Percentage distilled over, 42.1; Percentage distilled over within limits of original cut, 26.6.

a Not included in summary, Table 7.

SERIES 4.—REDISTILLATION OF CUTS (UBBELOHDE REDISTILLED IN UBBELOHDE) IN HEMPEL FLASK.

Cut, 100-125° C.; specific gravity, 0.723.			Cut, 125-150° C.; specific gravity, 0.742.			Cut, 150-175° C.; specific gravity, 0.756.			Cut, 175-200° C.; specific gravity, 0.768.			Cut, 200-225° C.; specific gravity, 0.779.			Cut, 225-250° C.; specific gravity, 0.790.			Cut, 250-275° C.; specific gravity, 0.801.		
Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.
80	2.1	0.681	105	2.2	0.724	135	4.3	0.743	160	7.6	0.759	180	3.4	0.768	210	8.8	0.780	235	7.4	0.787
85	2.1	.698	110	4.0	.728	140	10.6	.747	165	5.7	.763	185	7.9	.770	215	5.4	.782	240	7.0	.793
90	8.8	.709	115	12.4	.730	145	9.5	.750	170	10.3	.766	190	9.2	.771	220	7.8	.783	245	9.6	.796
95	6.5	.711	120	9.1	.733	150	8.5	.752	175	11.0	.766	195	8.2	.773	225	9.9	.785	250	9.5	.797
100	13.4	.716	125	9.7	.737	155	11.7	.754	180	11.9	.766	200	9.7	.773	230	9.5	.787	255	9.3	.798
105	13.5	.722	130	12.2	.739	160	9.7	.756	185	9.0	.767	205	9.2	.776	235	9.5	.788	260	10.5	.800
110	8.8	.724	135	9.6	.742	165	9.3	.757	190	8.0	.769	210	8.2	.777	240	8.6	.791	265	7.7	.802
115	7.9	.729	140	8.0	.746	170	8.1	.761	195	7.3	.770	215	7.1	.778	245	7.5	.793	270	6.8	.803
120	7.1	.731	145	7.3	.749	175	6.4	.763	200	5.6	.773	220	7.5	.781	250	6.2	.794	275	7.4	.806
125	7.7	.733	150	9.4	.752	180	5.0	.765	205	5.0	.773	225	5.4	.783	255	5.6	.796	280	3.5	.807
130	5.7	.736	155	5.4	.753	185	4.3	.766	210	4.7		230	5.5	.785	260	4.3	.798	285	4.4	.809
135	4.3	.737	160	3.1	.755							235	3.1	.789						
Residuum	10.1	.751		9.7	.763		11.8	.772		13.3	.785		13.9	.797		16.2	.806		16.9	.815
Maximum 25° cut:																				
Temperature limits, °C	85-110			110-135			135-160			165-180			185-210			215-240			240-265		
Percentage distilled over	51.0			53.0			50.0			50.2			44.5			45.3			46.6		
Percentage distilled over within limits of original cut	45.0			43.0			45.2			41.8			37.4			41.3			41.7		

TABLE 6.—*Results of redistillations of 25° fractions obtained in primary series of distillations*—Continued.

SERIES 5.—REDISTILLATION OF HEMPEL CUTS IN HEMPEL FLASK.

	Cut, 100–125° C.: specific gravity, 0.722.			Cut, 125–150° C.: specific gravity, 0.741.			Cut, 150–175° C.: specific gravity, 0.758.			Cut, 175–200° C.: specific gravity, 0.770.			Cut, 200–225° C.: specific gravity, 0.780.			Cut, 225–250° C.: specific gravity, 0.791.			Cut, 250–275° C.: specific gravity, 0.804.		
	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.	Temperature, °C.	Percentage redistilled.	Specific gravity of distillation cut.
	90	1.9	0.692	110	1.7	0.728	135	2.0	0.744	165	3.6	0.762	190	2.5	0.772	215	1.5	0.782	210	2.1	0.790
	95	3.3	.711	115	3.3	.733	140	6.6	.748	170	11.1	.763	195	8.5	.774	220	6.0	.787	215	4.1	.798
	100	11.1	.717	120	8.0	.737	145	9.1	.750	175	12.0	.765	200	11.5	.776	225	11.7	.788	250	10.3	.799
	105	14.1	.725	125	12.0	.741	150	11.3	.753	180	13.6	.767	205	12.4	.777	230	12.4	.789	255	13.3	.801
	110	10.8	.727	130	13.1	.743	155	11.5	.755	185	13.5	.768	210	14.6	.778	235	12.0	.790	260	14.2	.902
	115	10.3	.729	135	12.1	.745	160	12.1	.755	190	11.0	.768	215	12.6	.779	240	13.0	.792	265	11.9	.904
	120	10.3	.730	140	11.0	.748	165	13.5	.755	195	9.4	.770	220	9.3	.781	245	9.9	.794	270	11.5	.905
	125	8.1	.732	145	9.8	.751	170	10.5	.762	200	6.9	.773	225	8.8	.782	250	8.1	.795	275	9.7	.907
	130	6.4	.731	150	6.5	.753	175	8.2	.763	205	5.3	.773	230	6.6	.784	255	6.6	.796	280	6.6	.908
	135	4.2	.741	155	4.8	.755	180	6.3	.764	210	4.5	.777	235	4.8	.788	260	6.5	.800	285	5.4	.809
				160			185	4.3	.765												
Residuum		.7	.748		7.2	.763		8.6	.772		8.8	.786		9.8	.794		12.6	.805		10.9	.817
Maximum 25° cut:																					
Temperature limits, °C.	95–120			120–145			145–170			165–190			195–220			220–245			245–270		
Percentage distilled.	58.8			59.5			58.3			61.2			60.4			59.0			59.6		
Percentage distilled over within limits of original cut.	55.5			55.8			56.0			54.4			57.2			55.4			56.6		

TABLE 7.—*Summary of results of redistillation of 25° cuts obtained in primary distillations.*

[The detailed results of the redistillations are shown in Table 6.]

Original limits of cut, °C.	Original cut.				Maximum cut.							
	Percentage redistilled within original limits.				Temperature limits of maximum cuts, °C.				Percentage redistilled between limits of maximum cut.			
	Series 1.a	Series 2.b	Series 4.c	Series 5.d	Series 1.a	Series 2.b	Series 4.c	Series 5.d	Series 1.a	Series 2.b	Series 4.c	Series 5.d
100–125			45.0	55.5			85–110	95–120			51.0	58.8
125–150		25.8	43.0	55.8		105–130	110–135	120–145		34.5	53.0	59.5
150–175	14.1	26.2	45.2	56.0	95–120	140–165	135–160	145–170	24.7	29.3	50.0	58.3
175–200	13.4	23.8	41.8	54.4	125–150	150–175	165–190	165–190	22.6	34.1	50.2	61.2
200–225	13.2	24.4	37.4	57.2	150–175	175–200	185–210	195–220	21.7	31.2	44.5	60.4
225–250	14.9	24.1	41.3	55.4	170–195	205–230	215–240	220–245	19.0	31.0	45.3	59.0
250–275	14.9	23.7	41.7	56.6	205–230	225–250	240–265	245–270	19.8	33.3	46.6	59.6
275–300	14.6	24.2			235–260	255–280			20.3	28.8		
300–325	13.6				250–275				20.1			
Average	14.1	24.6	42.2	55.9					21.2	31.7	45.8	59.5

a Allen and Jacobs cuts redistilled in Hempel flask.
b Ubbelohde cuts redistilled in Hempel flask.
c Ubbelohde cuts redistilled in Ubbelohde flask, and then redistilled in Hempel flask. Results in series 3 are not comparable with those of the other four series.
d Hempel cut redistilled in Hempel flask.

In the results of series 1, Table 6, representing the Allen-Jacobs method, it will be noted that distillation began at a temperature nearly 100° C. below the lower limit of the original cut, and 18 to 20 per cent of the oil remained undistilled when the upper limit was reached, only about 14 per cent coming over between the original limits. This shows that when an oil is fractionated by the minimum-condensation method the original temperature limits of the various cuts are but remotely related to those discovered on redistillation.

The cuts from the Ubbelohde primary distillations (series 2 of Table 6) do not extend over quite so wide a range of temperature and gravity as do the ones represented in series 1. They do, however, indicate a considerable lack of homogeneity in the fractions obtained by the original distillation, as only about 25 per cent of each cut came over between the original limits.

The redistillation of Ubbelohde primary cuts in the Ubbelohde apparatus (series 3, Table 6) shows a higher degree of fractionation than that indicated in series 2. This difference illustrates the necessity of making all redistillations in one standard apparatus when figures for the comparison of different methods are desired. The 5° cuts in series 5, representing the redistillation of Hempel primary cuts in the Hempel apparatus, are larger than those appearing in series 3 and 4 and the ranges of temperature and specific gravity are narrower.

The Hempel cuts not only show a greater degree of homogeneity than is discovered for any of the other methods, but the maximum

25° cut was in every case but one obtained between limits only 5° lower than those of the primary distillation. About 55 per cent of each cut redistilled between the original limits. One distillation in the Hempel apparatus was found to be considerably more efficient than distillation and redistillation by the Ubbelohde method. The Ubbelohde method produces considerably sharper fractionation than that obtained by the use of the Allen and Jacobs still.

GENERAL DISCUSSION OF RESULTS OF DISTILLATIONS.

All the main points of interest from the various tables are summarized in Table 7, which is sufficient to show the wide differences among the degrees of separation attained by different methods of distillation. It is evident that the ideal distillation would be the one giving the largest possible maximum cut, the limits of which coincided with those of the primary distillation. Curves have been plotted to show the various relations.

PERCENTAGE AND TEMPERATURE.

Each of the curves in figures 10 and 11 represents an average for one of the methods of primary distillation. The percentage values were obtained by using the lower temperature limit of each cut as a basis and averaging the 5° fractions equally distant from this. Such a procedure may not be strictly logical, but it permits the drawing for each series of distillations of a single curve that represents with sufficient accuracy the characteristics of the method.

In figure 10 the cut represented is in each case that coming over below and not above the temperature represented. The ideal curve would be one entirely between the original temperature limits. Even the Hempel curve approaches this condition but distantly, though its superiority over the others is marked. Perhaps most impressive is the clear-cut demonstration of the fact that a single Hempel distillation gives a degree of fractionation considerably higher than that attained by two successive Ubbelohde distillations. This has been proven several times in the past, and the Hempel column studied by Young[a] was rated as equivalent to four open-flask distillations. The one used in the present experiments was probably equivalent to about three.

The curves in figure 11 were plotted from the same data as those used for figure 10, but summation values instead of individual cuts are represented. Here the ideal curve would be the one having the sharpest slope and the narrowest range on the axis of abcissas.

Figure 12 is a graphic representation of the results collected in Table 7.


[a] Young, Sydney, Op. cit., p. 179.
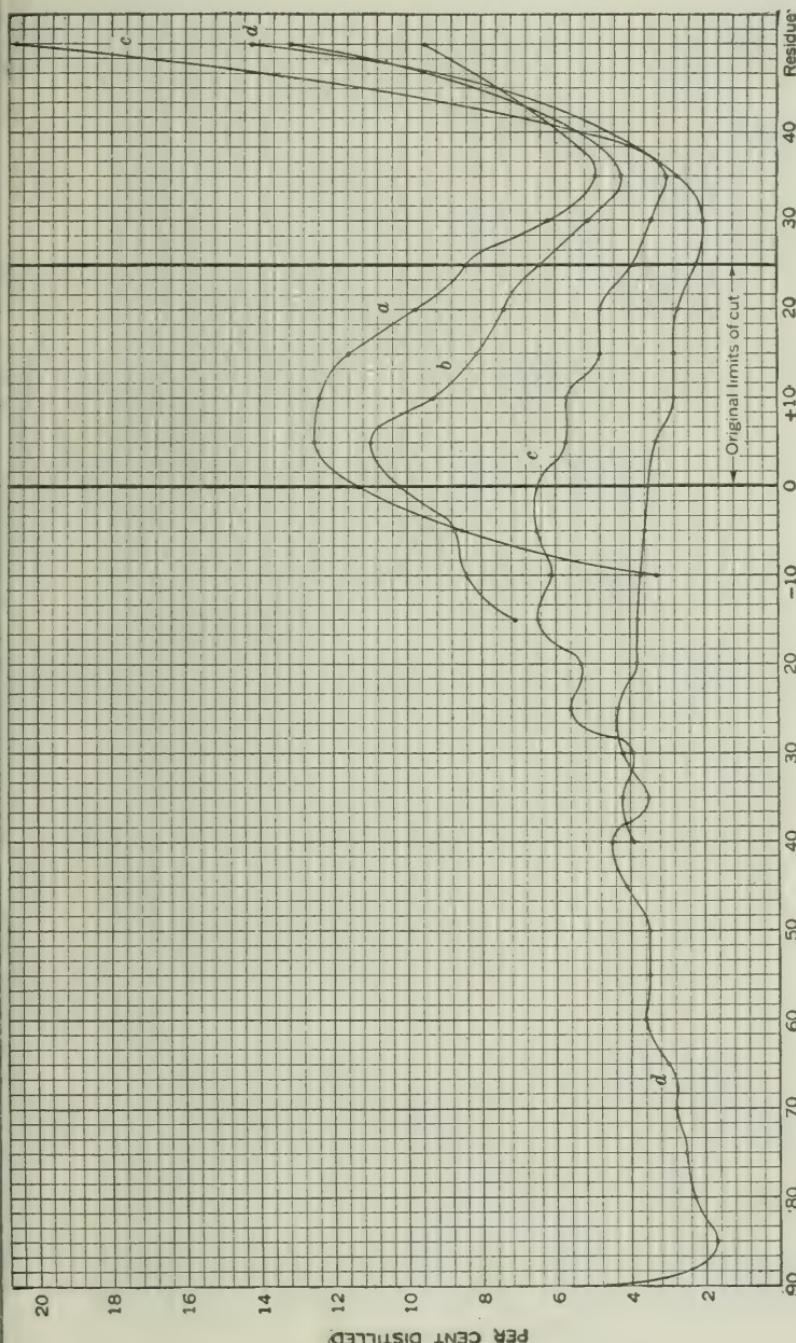
FIGURE 10.—Curves showing results of redistillations of cuts from several series of primary fractionations, and relations between temperature and magnitude of individual cuts; shortness of curve indicates efficiency of fractionation. *a*, Hempel cuts; *b*, Ubbelohde cuts; *c*, Ubbelohde cuts redistilled in Ubbelohde flask; *d*, Allen and Jacob cuts.

FIGURE 11.—Curves showing results of redistillation of cuts from series of primary fractionations, and relations between temperature and total amount distilled; steepness of slope indicates efficiency of fractionation. *a*, Hempel cuts; *b*, Ubbelohde cuts redistilled in Ubbelohde flask; *c*, Ubbelohde cuts; *d*, Allen and Jacobs cuts.

PERCENTAGE AND SPECIFIC GRAVITY.

The gravity measurements furnished a very exact index of the homogeneity of the 25° cuts of the original distillations. There appears to be no absolutely satisfactory way of obtaining average curves for each series; hence, typical single curves are given (fig. 13), each representing the relations between percentage and specific gravity
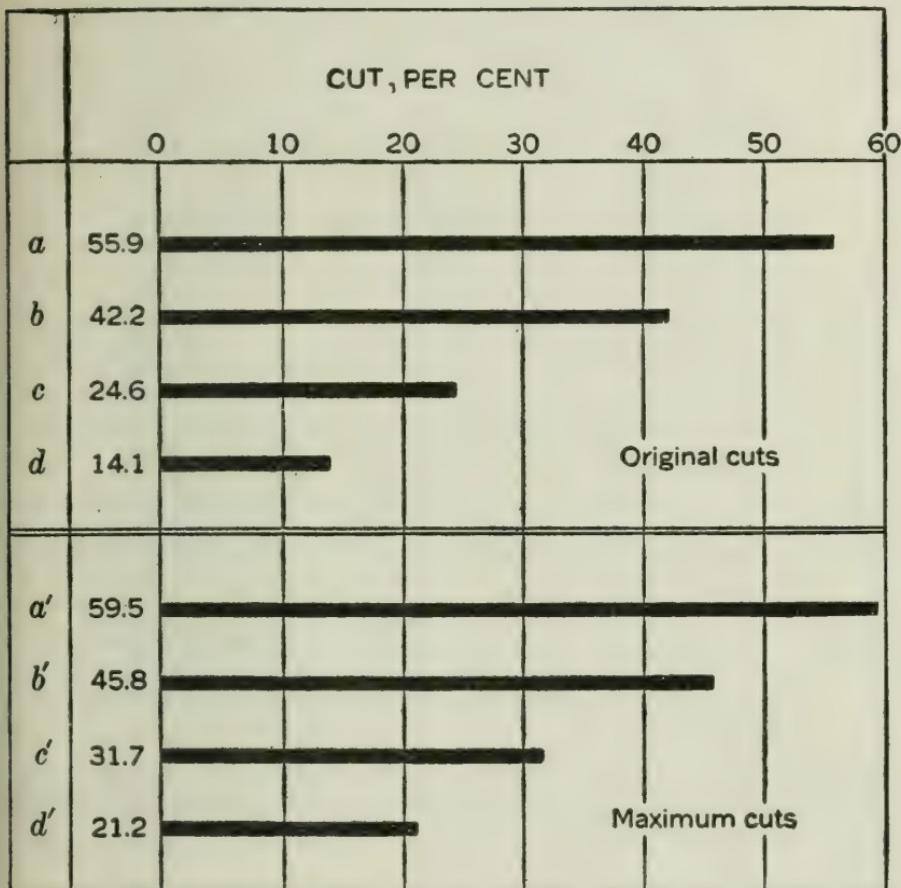
FIGURE 12.—Curves showing efficiency of various methods of distillation. *a* to *d,* percentage that redistilled between the original temperature limits; *a'* to *d',* maximum percentage distilling in any 25° temperature range of the redistillation. *a,* Hempel cuts; *b,* Ubbelohde cuts once redistilled; *c,* Ubbelohde cuts; *d,* Allen and Jacobs cuts.

that were discovered on redistilling the middle original cut of each series.

To put these curves on a comparable basis, each specific gravity was plotted relative to its difference from that measured for the original cut. The lines marking this value have been superimposed and used as the ordinate axis. The angle made by the average course of each of these curves with this axis indicates the homogeneity, or lack of

homogeneity, of the cut it represents. The superiority of the Hempel method is impressively shown when this factor is considered.

It happens that the relation of percentage and gravity can be shown clearly and completely by numbers, and Table 8 will be found instructive. The data given, obtained by interpolation on the curves,
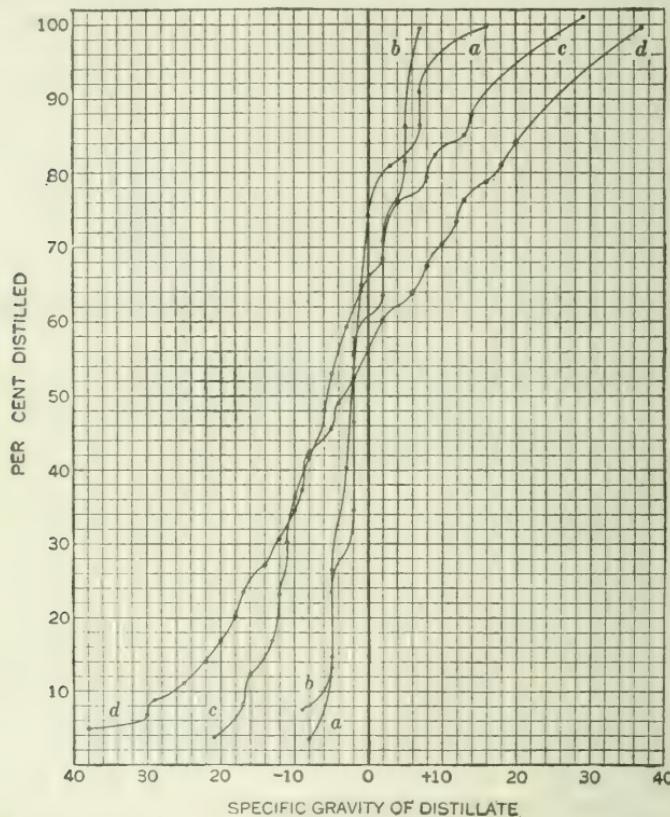
FIGURE 13.—Typical curves showing relations between percentage redistilled and specific gravity. Efficiency of fractionation is indicated by the closeness with which the curve approaches the vertical line used as the ordinate axis.

of which those in figure 13 are examples, represent increases in specific gravity between points marking 10 per cent and 85 per cent in the course of each redistillation. These particular points were chosen because they just avoided the irregular extremities of each of the curves.

TABLE 8.—*Range of specific gravity of cuts from primary series of distillations.*

[Values given represent increases between points marking 10 per cent and 85 per cent of the quantities distilling on redistillation.]

Tempera-ture limits of original cut, ° C.	Increase in specific gravity.			
	Primary distillation by Allen-Jacobs method.	Primary distillation by Ubbelohde method.	Ubbelohde primary cuts redistilled by Ubbelohde method.	Primary distillation by Hempel method.
100–125	....	....	0.029	0.024
125–150	....	0.047	.026	.018
150–175	0.075	.043	.020	.014
175–200	.058	.032	(.013)	.012
200–225	.052	.030	.018	.010
225–250	.047	.030	.018	.010
250–275	.050	.027	.020	.010
275–300	.044	.025	....	....
300–325	.043	....	....	....

Table 8 indicates a fact that does not appear on consideration of the percentage-temperature relations, namely, the degree of separation obtained by any particular method of distillation is not a constant and characteristic factor, but increases as the temperature scale is ascended. Redistillations increase in efficiency in a similar proportion. Consequently the conditions are such that measurements of continuously increasing value are being made by a method that varies in efficiency in very nearly the same ratio. By considering a relation that is independent of temperature one is able to detect and estimate the relative increase in efficiency of fractionation by the various methods. A closer study of Table 8 might bring out points of possible importance with regard to the mechanism of the various types of distillation methods: but it is sufficient to note that there are increases in efficiency as the temperature scale is ascended and that the maximum degree of separation attained by the Ubbelohde method is lower than the minimum of the Hempel.

CONCLUSIONS REGARDING THE EXPERIMENTS.

The obvious conclusion to be reached from the results of the experimental work just described is that the various classes of distillation methods differ considerably in efficiency. In the primary distillations the results of different methods show a superficial resemblance in the percentage-temperature and in the percentage and specific-gravity relations, but the results of the redistillation tests show that the differences are considerable. The average amounts distilling between the original limits were, for the typical methods of the three classes, 14 per cent, 25 per cent, and 56 per cent, respectively. A cut obtained by two successive distillations in the Ubbelohde apparatus yielded a 42 per cent fraction between the

original limits when redistilled in the more efficient Hempel apparatus. This indicates that the Hempel method, representative of maximum separation, was over two and perhaps even over three times as effective as the Ubbelohde method, which is representative of moderate separation. Still another important point is the fact that the upper temperature limit of the maximum 25° cut obtained on redistillation with the Hempel method was only 5° lower than the original limit, whereas with the Ubbelohde it was about 25° and with the Allen-Jacobs about 50° below the original limit.

These results indicate clearly the advantages of the method of maximum separation. The degree of efficiency attained by this method falls considerably short of 100 per cent, but it is still far greater than that of the open-flask method chosen as typical for the present work. In addition the temperature limits of the maximum-separation method represent very nearly the average volatility of the cut, whereas in the other methods the actual average is far below that indicated by these limits. This is made clear by the relations between the limits of the original cut and those of the maximum 25° cut. These advantages are so great that the fundamental desirability of the method of maximum separation seemed to have been established above question. Consequently it was deemed advisable to study the nature and magnitude of the differences in effect of various types of apparatus designed to attain efficient separation. As a result the experiments described in the following pages were performed.

EXPERIMENTS TO DETERMINE EFFICIENCY OF VARIOUS TYPES OF APPARATUS.

FACTORS TO BE CONSIDERED.

The previous experiments indicated that there were radical differences in the degrees of separation effected by typical methods from each of the three general classes. Qualitative indications of the differences were obtained through comparison of the figures from primary distillations, and quantitative results were obtained through several series of redistillations. It appeared that the qualitative indications were sufficiently clear-cut for general purposes of comparison, and it was, therefore, considered unnecessary to employ further the rather tedious method of redistillation.

It was found that the most impressive differences among results of primary distillations showed in the amounts distilling up to certain points not too high in the temperature scale. Thus with the Allen-Jacobs method the average amount distilling below 150° C. was 4.7 per cent, for the Ubbelohde method 13.2 per cent, and for the Hempel 15.5 per cent. It appeared possible, therefore, to differentiate among the degrees of efficiency attained by simply

noting the percentages distilling up to some temperature not too high.

An examination of the evidence already at hand pointed to but one conclusion—that a method yielding efficient separation is most desirable, provided it does not introduce too great mechanical difficulties. Methods of minimum separation have certain advantages, particularly for the distillation of emulsified products, but it must be realized that the fractionation effected by such methods is only approximate, and that the results obtained do not actually represent the volatility of the constituents of the products treated. It remains yet to be determined whether or not other methods are better for the treatment of products that are difficult to distill, but for the present the minimum-separation method appears to have advantages for such work.

The next step in this series of experiments was to compare the efficiencies of all the types of still heads that would be practicable for the use of petroleum technologists. On the basis of the evidence thus obtained it was possible to show the latitude allowable in the use of distilling apparatus and also the mechanical advantages of various types.

A final factor receiving consideration was that of cracking, which was shown not to be a serious drawback to the use of efficient fractionation. Indications were obtained regarding the temperature limits at which cracking becomes a factor of importance in distillation work.

METHOD OF MAKING TESTS.

The first task was to collect all the types of still heads that are available to petroleum chemists. All the forms listed in the catalogues of chemical supply houses were purchased, and in addition several types, not in general use but of theoretical importance, were made to order. A 10-gallon sample of Pennsylvania crude oil was obtained and kept under conditions which prevented changes in its composition. Portions of this oil were used for the various distillations.

For purposes of comparison distillations were also made with apparatus of the types yielding minimum and moderate separation. The Allen-Jacobs method, the retort, and the Lunge tar flask were used to represent in varying degree the method of minimum separation. The Engler-Ubbelohde and the simple distilling tube represented the class of moderate separation. For the method of efficient separation, still heads of the following types were used: Two-bulb Wurtz, four-bulb pear, twelve-bulb pear, De Konink, Norton-Otto, Glinsky, Young-Thomas dephlegmator, Le Bel-Henninger, Golodetz, Hempel, rod and disk, evaporator (modified).

In several instances the apparatus was constructed with bulb and fractionating column in one piece. Most of the still heads, however, were detachable and were employed in connection with a 500 c. c. Kjeldahl flask that had been so modified (see Pl. I) as to permit the easy measurement of temperatures of the liquid oil. The cork joints between the distilling bulb and the fractionating column proved troublesome, but it was found that by using proper care they could be made tight with a paste of litharge and glycerin. The corks were carefully bored and fitted and then coated with a thick paste, made with specially dried lead oxide that had been treated in a furnace for three-quarters of an hour at a temperature of 600° C. One-half hour was allowed for the paste to harden before the distillation was begun and in that time it set sufficiently to make an oil-tight seal which held even when the cork itself was practically reduced to coke. The chief danger of leakage was from swelling of the cork during the distillation, with consequent cracking of the coating of lead oxide and glycerin. This was prevented by thoroughly heating the cork and charring its surface before using. It was generally necessary to use a fresh cork for each distillation as at the temperatures attained at the base of the distilling column the cork was pretty thoroughly decomposed. The whole procedure, though necessary, was troublesome and emphasized thoroughly the undesirability of using cork joints for high-temperature distillation work.

RESULTS OF TESTS.

The results obtained by the use of the individual stills are shown in Table 9, and are summarized in Table 10. The detailed results are of little interest unless it is desired to learn the characteristic behavior of any special still. Specific-gravity figures have been obtained in all cases, but do not seem to be particularly instructive, except as they fail to show variations. Of more importance are the figures for average variations in the percentage cuts of duplicate distillations, which indicate, in a general way, the readiness with which checks may be obtained in the laboratory work. It will be noted that the differences among these figures are not striking except in the case of the distillations with the retort, in which results of entirely different character were obtained by slightly varying the position of the thermometer bulb. The average variations were least in the results of the Allen-Jacobs methods and two of the methods requiring the use of efficient fractionating columns—namely, the Hempel, and the Young-Thomas dephlegmator. The close agreement for results with the dephlegmator may be accidental, but the Hempel undoubtedly owes the uniformity of the results it yields to its large heat capacity, which makes it insensitive to changes in the temperature of the room, air currents, and any of the other factors that make for irregularity.
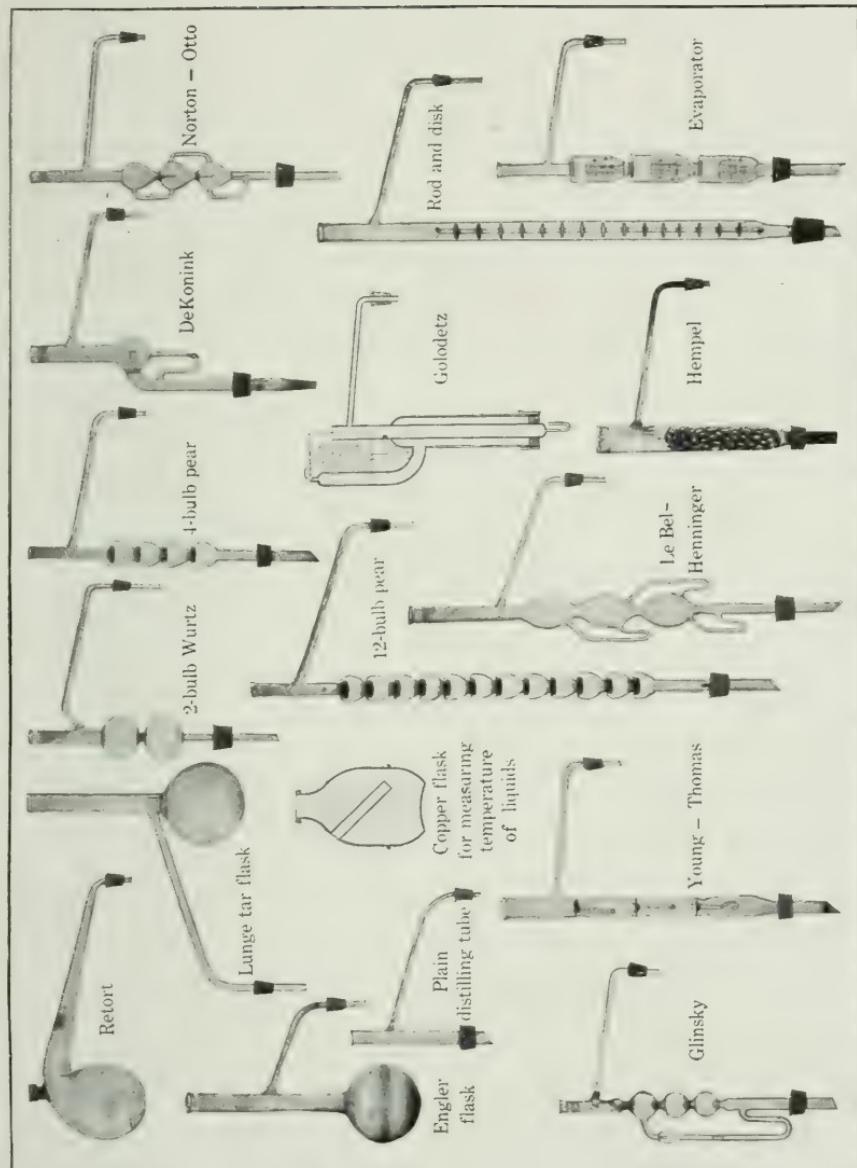
TYPES OF STILL HEADS STUDIED.
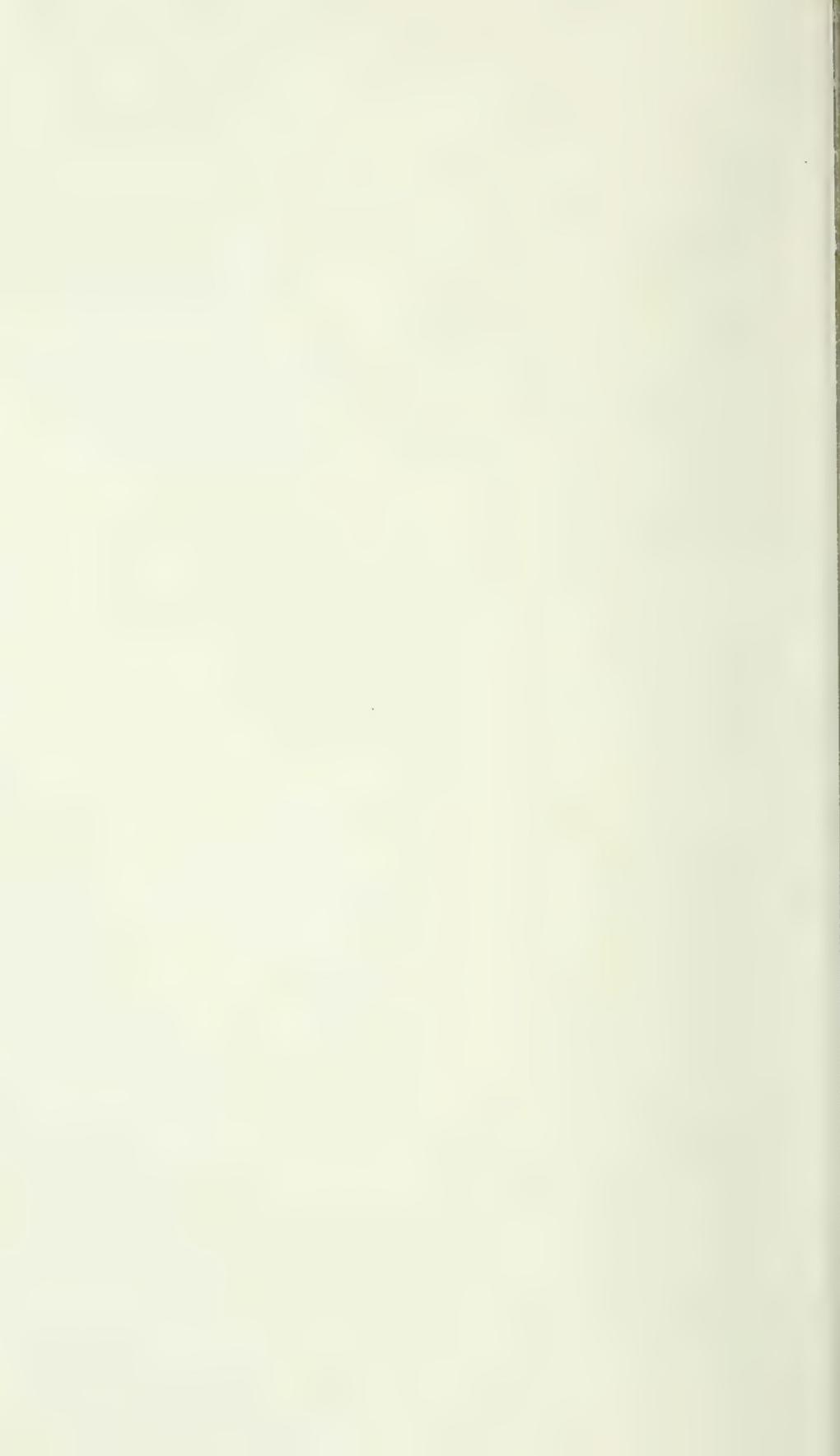
TABLE 9.—*Results of distillations of uniform sample of Pennsylvania crude oil in various types of apparatus.*

[Per cent columns show percentage distilled, specific gravity columns show specific gravity of distillation cut; typical distillations are indicated by letters A, B, C, etc. Figures for average variations in percentage distilled in duplicate analyses are shown. See also Table 10.]

(1) ALLEN-JACOBS.

Temperature, °C.	Per cent.				Specific gravity.			
	A.	B.	C.	Average.	A.	B.	C.	Average.
125	0.9	1.0	1.0	1.0	....	....	....	....
150	4.9	5.2	4.9	5.0	0.708	0.709	0.707	0.708
175	7.7	7.5	7.8	7.6	.732	.734	.733	.733
200	7.7	7.9	7.8	7.8	.753	.754	.752	.753
225	7.6	7.4	7.5	7.5	.766	.767	.768	.767
250	7.1	7.1	6.8	7.0	.778	.779	.780	.779
275	6.5	6.7	7.0	6.7	.789	.790	.789	.789
300	6.5	6.3	5.9	6.2	.799	.800	.800	.800
325	6.2	6.6	6.9	6.6	.809	.811	.811	.810
Average variation				2.1				

(2) RETORT AND (3) LUNGE TAR FLASK.

Temperature °C.	(2) Retort a (250 c. c.).						(3) Lunge tar flask.a							
	Thermometer bulb immersed in liquid.		Thermometer bulb just below outlet.		Thermometer bulb at middle of outlet.		Per cent.				Specific gravity.			
	Per cent.	Specific gravity.	Per cent.	Specific gravity.	Per cent.	Specific gravity.	A.	B.	C.	Average.	A.	B.	C.	Average.
100	0.0	......	0.5	......	2.1	0.689	0.8	0.7	1.6	1.0	......	......	......	......
125	.8	......	2.5	0.691	4.5	.729	3.8	3.9	4.2	4.0	0.699	0.696	0.706	0.700
150	4.1	0.701	8.7	.724	7.6	.733	7.7	7.7	7.7	7.7	.727	.727	.730	.728
175	7.0	.729	8.3	.747	10.0	.756	7.8	9.1	8.4	8.4	.748	.747	.751	.749
200	7.3	.747	8.3	.764	11.0	.773	8.4	6.8	7.8	7.6	.765	.763	.767	.765
225	7.0	.762	8.3	.780	6.7	.789	5.8	7.8	7.4	7.0	.777	.777	.780	.778
250	6.5	.773	6.8	.792	8.0	.798	7.3	6.2	6.1	6.5	.787	.789	.793	.790
275	6.0	.784	6.5	.804	9.1	.816	6.1	6.3	6.5	6.3	.797	.799	.802	.799
300	8.1	.797	7.4	.815	7.3	.827	7.4	7.3	7.5	7.4	.810	.811	.814	.812
Average variation										5.9				

a Purchased from chemical supply house.

(4) UBBELOHDE-ENGLER (MODIFIED a).

Temperature °C.	Per cent.					Specific gravity.				
	A.	B.	C.	D.	Average.	A.	B.	C.	D.	Average.
100	2.6	2.7	3.0	3.0	2.8	0.678	0.683	0.683	0.683	0.682
125	5.1	5.7	5.3	5.5	5.4	.712	.713	.715	.714	.713
150	7.9	7.7	7.6	7.8	7.7	.737	.738	.738	.739	.738
175	7.2	7.9	7.6	7.0	7.4	.755	.757	.756	.757	.756
200	6.8	6.9	7.4	7.5	7.1	.769	.770	.771	.772	.771
225	7.1	6.9	6.7	7.1	7.0	.782	.783	.782	.783	.782
250	6.8	7.3	6.7	6.8	6.8	.794	.795	.794	.794	.794
275	6.7	7.1	6.5	7.1	6.8	.804	.806	.805	.805	.805
Average variation					3.3					

a See page 31.

TABLE 9.—*Results of distillations of uniform sample of Pennsylvania crude oil in various types of apparatus*—Continued.

(5) PLAIN DISTILLING TUBE AND (6) TWO-BULB WÜRTZ.

Temperature, °C.	(5) Plain distilling tube.a [Height, flask to outlet, 3 inches.]								(6) Two-bulb Würtz.a [Height, flask to outlet, 6 inches.]	
	Per cent.				Specific gravity.				Per cent.	Specific gravity.
	A.	B.	C.	Average.	A.	B.	C.	Average.		
100..............	3.2	2.8	3.2	3.1	0.683	0.688	0.685	0.685	4.4	0.680
125..............	4.8	4.9	4.8	4.8	.714	.715	.715	.715	5.3	.718
150..............	7.5	7.3	7.3	7.4	.738	.737	.737	.737	7.0	.741
175..............	8.0	8.0	8.4	8.1	.757	.755	.756	.756	(b)	(b)
200..............	7.9	7.5	7.2	7.5	.771	.769	.770	.770	....	....
225..............	6.6	6.9	7.3	6.9	.782	.781	.782	.782	....	....
250..............	7.0	7.5	6.6	7.0	.795	.793	.794	.794	....	....
275..............	7.2	7.3	7.1	7.2	.806	.804	.806	.805	....	....
Average variation........................				2.5						

a Purchased from chemical supply house.
b Column flooded owing to small bore of tube from flask to first bulb.

(7) FOUR-BULB PEAR AND (8) NORTON AND OTTO.

Temperature, °C.	(7) Four-bulb pear.a [Height, flask to outlet, 9 inches.]								(8) Norton–Otto.a [Height, flask to outlet, 9 inches.]	
	Per cent.				Specific gravity.				Per cent.	Specific gravity.
	A.	B.	C.	Average.	A.	B.	C.	Average.		
100..............	4.3	4.3	4.5	4.4	0.681	0.681	0.680	0.681	4.9	0.683
125..............	5.7	5.1	5.8	5.5	.722	.722	.722	.722	5.7	.726
150..............	8.5	9.2	8.0	8.5	.745	.744	.743	.744	6.7	.744
175..............	7.0	7.0	7.3	7.1	.761	.764	.760	.762	6.8	.760
200..............	6.1	6.7	6.6	6.5	.773	.775	.773	.774	7.2	.773
225..............	6.2	6.2	5.8	6.1	.784	.786	.783	.784	(b)	(b)
250..............	7.2	6.2	6.7	6.7	.794	.795	.793	.794	....	....
275..............	7.2	6.6	7.3	7.0	.807	.806	.805	.806	....	....
Average variation........................				3.8						

a Purchased from chemical supply house.
b Column flooded owing to narrowness of tubes.

TABLE 9.—*Results of distillations of uniform sample of Pennsylvania crude oil in various types of apparatus*—Continued.

(9) DE KONINK AND (10) TWELVE-BULB PEAR.

Temperature, °C.	(9) De Konink.[a] [Height, flask to outlet, 8 inches.]								(10) Twelve-bulb pear.[a] [Height, flask to outlet, 18 inches.]	
	Per cent.				Specific gravity.				Per cent.	Specific gravity.
	A.	B.	C.	Average.	A.	B.	C.	Average.		
100	4.5	4.9	4.9	4.8	0.682	0.682	0.682	0.682	5.7	0.682
125	5.6	5.5	5.7	5.6	.722	.727	.721	.723	6.7	.731
150	7.1	6.7	7.0	6.9	.744	.745	.744	.744	6.1	.749
175	6.4	7.0	6.8	6.7	.759	.759	.758	.759	7.1	.764
200	6.9	7.5	6.7	7.0	.770	.771	.772	.771	7.0	.776
225	6.9	6.3	6.5	6.6	.782	.782	.782	.782	6.1	.785
250	6.5	6.5	7.0	6.6	.792	.793	.793	.793	(b)	(b)
275	7.0	7.1	6.8	7.0	.805	.806	.805	.805		
Average variation				2.9						

[a] Purchased from chemical supply house.
[b] The column flooded owing to excessive reflux condensation.

(11) GLINSKY AND (12) LE BEL-HENNINGER.

Temperature, °C.	(11) Glinsky, with glass valves.[a] [Height, flask to outlet, 9 inches.]								(12) Le Bel-Henninger.[a] [Height, flask to outlet, 12 inches.]	
	Per cent.				Specific gravity.				Per cent.	Specific gravity.
	A.	B.	C.	Average.	A.	B.	C.	Average.		
100	5.6	5.9	5.2	5.6	0.686	0.688	0.681	0.685	5.9	0.684
125	5.9	6.1	5.4	5.8	.725	.726	.723	.725	5.8	.730
150	6.8	7.7	8.2	7.6	.746	.748	.746	.747	7.0	.749
175	6.9	7.1	7.3	7.1	.759	.762	.761	.761	6.1	.763
200	5.8	6.3	6.6	6.2	.772	.775	.774	.774	6.7	.775
225	6.8	6.7	6.8	6.8	.783	.785	.785	.784	(b)	(b)
250	6.2	7.4	6.2	6.6	.793	.797	.795	.795		
275	6.6	6.7	7.2	6.8	.805	.810	.808	.808		
Average variation				4.1						

[a] Purchased from chemical supply house.
[b] Column flooded and stopped distillation.

TABLE 9.—*Results of distillations of uniform sample of Pennsylvania crude oil in various types of apparatus*—Continued.

(13) YOUNG AND THOMAS, AND (14) GOLODETZ.

Temperature, °C.	(13) Young-Thomas dephlegmator.[a] [Height, flask to outlet, 10 inches.]								(14) Golodetz.[b] [Height, flask to outlet, 8 inches.]	
	Per cent.				Specific gravity.				Per cent.	Specific gravity.
	A.	B.	C.	Average.	A.	B.	C.	Average.		
100	5.9	5.6	5.6	5.7	0.684	0.682	0.682	0.683	6.2	0.682
125	5.8	5.6	6.1	5.8	.731	.730	.730	.730	5.7	.732
150	6.3	6.3	5.9	6.2	.747	.747	.747	.747	6.4	.748
175	6.7	6.7	6.7	6.7	.763	.763	.763	.763	8.0	.765
200	6.8	6.8	6.4	6.7	.773	.772	.772	.772	7.9	.777
225	6.3	6.3	6.7	6.4	.784	.782	.783	.783	8.5	.792
250	6.1	6.3	6.2	6.2	.794	.794	.794	.794	8.0	.804
275	6.8	7.1	[6.0]	6.9	.806	.805	.805	.805	(c)	(c)
Average variation				1.9						

[a] Made to special order.
[b] Copper, made to special order.
[c] Results abnormal. Strong indications of cracking (see p. 60).

(15) HEMPEL.[a]

[Height, flask to outlet, 6 inches.]

Temperature, °C.	Per cent.							Specific gravity.						
	A.	B.	C.	D.	E.	F.	Average.	A.	B.	C.	D.	E.	F.	Average.
100	6.2	6.5	5.9	6.1	6.5	6.3	6.3	0.698	0.695	0.696	0.694	0.689	0.684	0.693
125	6.4	6.0	6.5	6.4	6.2	6.1	6.3	.733	.732	.732	.732	.731	.730	.732
150	5.6	6.2	5.9	5.9	6.2	6.3	6.0	.751	.748	.747	.747	.747	.746	.747
175	7.0	6.9	6.7	7.0	6.7	6.7	6.8	.764	.762	.762	.762	.762	.761	.762
200	6.2	6.2	6.3	6.4	6.4	6.5	6.3	.775	.773	.773	.772	.772	.774	.773
225	6.5	6.4	6.4	6.0	6.5	6.4	6.4	.785	.783	.783	.782	.783	.783	.783
250	6.9	6.1	6.5	6.4	6.5	6.5	6.5	.796	.793	.794	.794	.794	.793	.794
275	5.5	7.0	6.9	7.1	7.2	6.8	7.0	.806	.804	.806	.806	.805	.805	.805
Average variation							2.2							

[a] Diameter, 1 inch; depth of beads, 5 inches; made to special order.

(16) ROD AND DISK, AND (17) THREE-SECTION EVAPORATOR.

Temperature, °C.	(16) Rod and disk[a] (height, flask to outlet, 18 inches).		(17) Three-section evaporator[b] (height, flask to outlet, 10 inches).									
	Per cent.	Specific gravity.	Per cent.					Specific gravity.				
			A.	B.	C.	D.	Average.	A.	B.	C.	D.	Average.
100	6.5	0.685	6.2	6.9	6.5	6.7	6.6	0.684	0.687	0.687	0.687	0.686
125	5.9	.732	5.4	6.8	6.0	6.0	6.0	.729	.734	.731	.732	.731
150	6.4	.749	6.7	6.3	7.4	6.5	6.7	.749	.752	.751	.751	.751
175	7.0	.764	7.2	7.0	7.1	7.1	7.1	.761	.766	.765	.763	.764
200	6.3	.775	6.4	5.6	6.9	6.5	6.3	.774	.775	.776	.775	.775
225	6.5	.785	6.4	6.4	5.1	6.6	6.1	.783	.784	.783	.785	.784
250	7.1	.797	6.7	6.6	6.9	6.4	6.7	.795	.792	.792	.792	.793
275	(c)	(c)	7.1	6.9	6.5		6.9	.807	.808	.808	.806	.807
Average variation							4.3					

[a] Purchased from chemical supply house.
[b] Made to special order.
[c] Distillation stopped by excessive reflux condensation.

TABLE 10.—*Summary of results of distilling Pennsylvania crude oil in various types of apparatus, showing average percentage distilled at temperatures of 100° to 325° C.*

Series No.[a]	Type of apparatus.	Average percentage distilled.										
		100° C.	125° C.	150° C.	175° C.	200° C.	225° C.	250° C.	275° C.	300° C.	325° C.	Up to 150° C.
1	Allen-Jacobs	0.0	1.0	5.0	7.6	7.8	7.5	7.0	6.7	6.2	6.6	6.0
2	Retort (B)	0.5	2.5	8.7	8.3	8.3	8.3	6.8	6.5	7.4	.....	11.7
3	Lunge	1.0	4.0	7.4	8.4	7.6	7.0	6.5	6.3	7.4	.....	12.4
4	Engler-Ubbelohde	2.8	5.4	7.7	7.4	7.1	7.0	6.9	6.8	.....	.....	15.9
5	Plain distilling tube	3.1	4.8	7.4	8.1	7.5	6.9	7.0	7.2	.....	.....	15.3
6	Two-bulb Wurtz	4.4	5.3	7.0	.....	.....	.....	.....	.....	.....	.....	16.7
7	Four-bulb pear	4.4	5.5	8.5	7.1	6.5	6.1	6.7	7.0	.....	.....	18.4
8	Norton-Otto	4.9	5.7	6.7	6.8	7.2	.....	.....	.....	.....	.....	17.3
9	De Koninck	4.8	5.6	6.9	6.7	7.0	6.6	6.6	7.0	.....	.....	17.3
10	Twelve-bulb pear	5.7	6.7	6.1	7.1	7.0	6.1	.....	.....	.....	.....	18.5
11	Glinsky	5.6	5.8	7.6	7.1	6.2	6.8	6.6	6.8	.....	.....	19.0
12	Le Bel-Henninger	5.9	5.8	7.0	6.1	6.7	.....	.....	.....	.....	.....	18.7
13	Young-Thomas	5.7	5.8	6.2	6.7	6.7	6.4	6.2	6.9	.....	.....	17.7
14	Golodetz	6.2	5.7	6.4	8.0	7.9	8.5	8.0	.....	.....	.....	18.3
15	Six-inch Hempel	6.3	6.3	6.0	6.8	6.3	6.4	6.5	7.0	.....	.....	18.6
16	Rod and disk	6.5	5.9	6.4	7.0	6.3	6.5	7.1	.....	.....	.....	18.8
17	Evaporator	6.6	6.0	6.7	7.1	6.3	6.1	6.7	6.9	.....	.....	19.3

a See Table 9 for detailed results.

DISCUSSION OF RESULTS OF TESTS.

A study of Table 10 and of figure 14 shows that when comparisons are made on the basis of the magnitude of the first cut, a number of
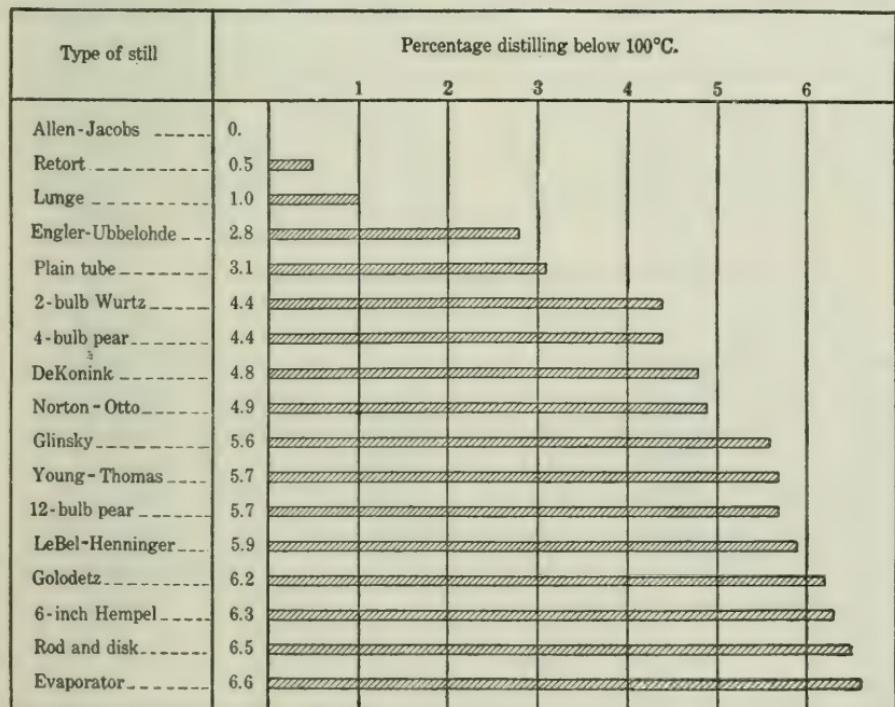
FIGURE 14.—Diagram showing relative magnitude of cuts to 100° C. obtained by the use of various types of distilling apparatus. Note that with several methods the efficiency of separation is about the same.

the still heads are found to be practically equal in efficiency. Still heads represented by series 10 to 17 of Table 9 are sufficiently alike so that choice may be made among them by considering other factors than the degree of efficiency attained. The 12-bulb pear, the rod and disk, and the Le Bel-Henninger apparatus are immediately eliminated for petroleum because they fail to permit the passage of vapor when higher temperatures are reached. The Golodetz, which on theoretical grounds seems particularly desirable, behaves in an abnormal manner with regard to the size of the cuts above 175° C. Much work was done with this still on another sample of oil, but reliable results could not be obtained.

The Young-Thomas apparatus and the evaporator have many theoretical and practical advantages,[a] but they are not available on the market and are rather fragile and complicated. The Glinsky is a little less efficient, and although it can be easily purchased is fragile and costly. All indications seem to point to the Hempel apparatus as the most promising; and, from the results of these experiments, it seems to be in a class by itself. Its one inherent advantage is the amount of "phlegm," or condensed vapor, held up by the mass of beads. This has not, however, been found to interfere seriously in distillations of initial charges of 100 grams or more. Other advantages of the Hempel still head are that the apparatus is efficient, cheap, readily available or improvisable, easy to manipulate and clean, and permits the elimination of the troublesome cork joint between the distilling bulb and the fractionating column. None of the other types possesses this advantage except the pear and the rod-and-disk. Both of these however, fail in efficiency unless they are of excessive length, and then too much condensation results and the stills fail to work through the necessary range of temperature.

EXPERIMENTS WITH HEMPEL COLUMNS.

As the experiments showed that the Hempel column seemed, for mechanical reasons, to be the most favorable type of still head for use in the fractionation of petroleum, it was decided to study thoroughly the effect of varying the dimensions and construction of the column. The following details were considered: (1) Effect of height of column; (2) effect of diameter of column; (3) effect of mechanical details, such as filling material, shape, size, and material of bulb and material of column. The various shapes of column tested are shown in figure 15.

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[a] Young, Sidney, Op. cit., pp. 154–179.
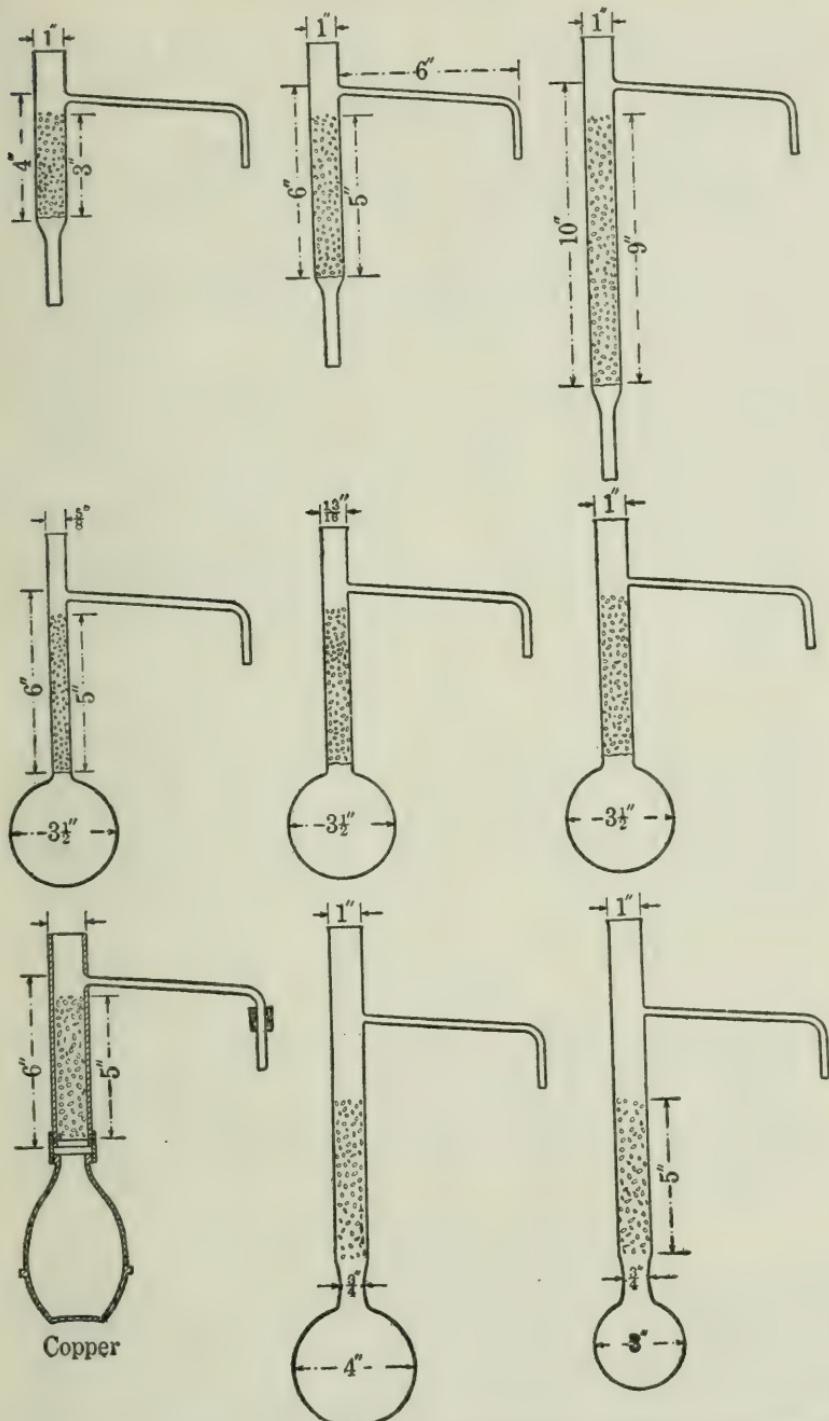
FIGURE 15.—Various types of Hempel columns of which the degrees of efficiency were studied.

EFFECT OF HEIGHT.

Three Hempel columns were obtained. These were 1 inch in diameter, 4, 6, and 10 inches in height from constriction to outlet tube, and held a column of aluminum beads 3, 5, and 9 inches in height, respectively. The still heads were used in connection with the copper flask described on page 54. The results of the distillations with these columns are shown in Table 11.

TABLE 11.—*Results of distillations of uniform sample of Pennsylvania crude oil* [a] *with 1-inch Hempel columns of different heights.*

FOUR-INCH COLUMN.

Tempera-ture, °C.	Per cent distilled.							Specific gravity of distillation.						
	A.	B.	C.	D.	E.	F.	Av.	A.	B.	C.	D.	E.	F.	Av.
100	5.7	5.9	5.9	[7.0]	5.6	......	5.8	0.690	0.692	0.691	0.687	0.687	......	0.689
125	6.1	6.2	6.4	6.3	5.8	......	6.2	.730	.730	.730	.733	.731	......	.731
150	6.2	6.5	7.0	6.4	6.1	......	6.4	.748	.747	.746	.748	.747	......	.747
175	7.0	6.6	6.6	6.7	6.9	......	6.8	.761	.762	.762	.762	.761	......	.762
200	6.2	6.4	6.3	6.4	6.2	......	6.3	.773	.772	.772	.773	.772	......	.772
225	6.3	6.7	6.2	6.2	6.7	......	6.4	.783	.782	.783	.783	.782	......	.783
250	6.5	6.3	6.4	6.5	6.2	......	6.4	.792	.794	.794	.793	.793	......	.793
275	7.3	7.3	7.2	6.7	7.1	......	7.1	.806	.805	.805	.806	.805	......	.805
Average variation......................							2.4							

SIX-INCH COLUMN.

Temp.	A	B	C	D	E	F	Av	A	B	C	D	E	F	Av
100	6.2	6.5	5.9	6.1	6.5	6.3	6.3	0.698	0.695	0.696	0.694	0.689	0.684	0.693
125	6.4	6.0	6.5	6.4	6.2	6.1	6.3	.733	.732	.732	.732	.731	.730	.732
150	5.6	6.2	5.9	5.9	6.2	6.3	6.0	.751	.748	.747	.747	.747	.746	.747
175	7.0	6.9	6.7	7.0	6.7	6.7	6.8	.764	.762	.762	.762	.762	.761	.762
200	6.2	6.2	6.3	6.4	6.4	6.5	6.3	.775	.773	.773	.772	.772	.774	.773
225	6.5	6.4	6.4	6.0	6.5	6.4	6.4	.785	.783	.783	.783	.782	.783	.783
250	6.9	6.1	6.5	6.4	6.5	6.5	6.5	.796	.793	.794	.794	.794	.793	.794
275	[5.5]	7.0	6.9	7.1	7.2	6.8	7.0	.806	.804	.806	.806	.805	.805	.805
Average variation..............							2.2							

TEN-INCH COLUMN.

Temp.	A	B	C	D	E	F	Av	A	B	C	D	E	F	Av
100	6.3	6.3	7.0	6.9	7.3	6.7	6.7	0.688	0.692	0.687	0.685	......	0.684	0.687
125	5.9	6.3	6.3	6.3	6.3	5.8	6.2	.732	.733	.732	.731	......	.728	.731
150	6.1	5.8	6.3	6.8	6.2	6.0	6.2	.746	.749	.748	.748	......	.745	.747
175	6.7	6.5	6.8	6.9	6.9	6.9	6.8	.762	.762	.763	.762	......	.759	.762
200	6.1	6.2	6.1	6.2	6.5	6.3	6.2	.772	.772	.772	.773	......	.772	.772
225	6.4	6.5	6.5	6.5	......	......	6.5	.782	.782	.783	.783	......	......	.783
250	6.8	6.6	6.8	6.4	......	......	6.6	.793	.794	.794	.793	......	......	.793
275	7.1	7.3	7.1	7.4	......	......	7.2	.804	.806	.806	.807	......	......	.806
Average variation......................							2.4							

[a] Same sample as that used for experiments of Table 9.

The column for average percentages in Table 11 brings out the fact that when vapors pass through a fractionating column of the Hempel type at the moderate rate at which laboratory distillations are conducted they come very nearly to equilibrium with the condensed liquid after passing through a comparatively short length of the filling material. Increasing the length of the column as much as 200 per cent did not materially affect the results obtained, as the efficiency of the 10-inch column was about the same as that of the

4-inch. The 10-inch column was unwieldy and produced too much condensation at higher temperatures; the 4-inch tended to be unreliable unless the rate of distillation was regulated with much care.

EFFECT OF DIAMETER.

As a 6-inch column with 5 inches of beads seemed to be an optimum with regard to the factor of height, the next experiments were in regard to diameter. Distillations were run with three 6-inch columns, respectively $\frac{5}{8}$ inch, $\frac{13}{16}$ inch, and 1 inch in diameter. These columns were sealed directly on glass bulbs and were made without any constriction at the base of the column for reasons set forth in a subsequent discussion of mechanical advantages and possibilities. The results in Table 12 indicate that the effect of diameter on the efficiency of a Hempel column used in petroleum distillation is slight, the differences being about the same as those among figures for still heads of various heights.

TABLE 12.—*Results of distillations of uniform sample of Pennsylvania crude oil* [a] *with Hempel columns 6 inches high and of different diameters.*

COLUMN $\frac{5}{8}$ INCH IN DIAMETER.

Temperature °C.	Percentages distilled.						Specific gravity.					
	A.	B.	C.	D.	E.	Av.	A.	B.	C.	D.	E.	Av.
100	5.9	6.0	5.9	......	......	5.9	0.681	0.685	0.685	......	......	0.684
125	6.4	6.1	5.7	......	......	6.1	.729	.730	.731	......	......	.730
150	6.9	6.7	6.4	......	......	6.6	.744	.757	.748	......	......	.747
175	6.9	7.2	7.3	......	......	7.1	.758	.761	.762	......	......	.760
200	6.6	6.7	6.6	......	......	6.6	.771	.775	.772	......	......	.773
225	6.0	6.2	6.2	......	......	6.2	.781	.785	.784	......	......	.783
250	7.0	6.9	6.7	......	......	6.9	.792	.795	.794	......	......	.794
275	......	......	7.0	......	......	7.0	......	......	.809	......	......	.809

Average cut, 6.3 per cent; average variation in similar cuts, 1.9 per cent.

COLUMN $\frac{13}{16}$ INCH IN DIAMETER.

Temperature °C.	Percentages distilled.						Specific gravity.					
	A.	B.	C.	D.	E.	Av.	A.	B.	C.	D.	E.	Av.
100	5.9	5.5	6.0	5.9	......	5.8	0.684	0.682	0.683	0.684	......	0.683
125	6.5	6.1	6.3	6.0	......	6.2	.730	.730	.728	.730	......	.730
150	6.2	6.1	5.8	6.1	......	6.1	.749	.748	.745	.746	......	.747
175	6.8	7.0	6.7	6.6	......	6.8	.762	.762	.762	.761	......	.762
200	6.1	6.3	6.7	7.0	......	6.5	.774	.773	.772	.772	......	.773
225	6.5	6.2	6.2	6.0	......	6.2	.784	.783	.782	.783	......	.783
250	6.6	6.7	6.5	6.5	......	6.6	.795	.795	.793	.794	......	.794
275	6.4	5.9	6.1	6.0	......	6.1	.806	.805	.804	.804	......	.805
300	6.5	6.5	......	......	......	6.5	.815	.816	......	.815	......	.815

Average cut, 6.3 per cent; average variation in similar cuts, 2.1 per cent

COLUMN 1 INCH IN DIAMETER.

Temperature °C.	Percentages distilled.						Specific gravity.					
	A.	B.	C.	D.	E.	Av.	A.	B.	C.	D.	E.	Av.
100	6.2	5.9	6.1	5.7	5.8	5.9	0.687	0.683	0.685	0.683	0.683	0.684
125	5.9	6.3	6.1	6.0	6.5	6.2	.733	.731	.734	.730	.731	.732
150	6.2	6.4	6.3	6.1	6.1	6.2	.749	.747	.747	.747	.747	.747
175	6.4	6.3	6.4	6.9	6.7	6.5	.763	.763	.763	.762	.763	.763
200	6.7	6.6	6.8	6.7	6.1	6.6	.773	.773	.774	.772	.772	.773
225	6.0	6.4	6.2	6.1	6.5	6.2	.783	.784	.784	.782	.784	.783
250	6.4	6.3	6.4	6.6	6.5	6.4	.795	.794	.795	.793	.795	.794
275	6.2	6.4	6.0	6.2	6.2	6.2	.805	.806	.806	.804	.805	.805
300	6.6	6.3	6.7	6.8	6.7	6.6	.816	.816	.816	.817	.816	.816

Average cut, 6.3 per cent; average variation in similar cuts, 2.2 per cent.

[a] Same sample as that used for experiments of Tables 9 and 10.

EFFECT OF MECHANICAL DETAILS.

After it had been demonstrated that for petroleum distillation the results attained with Hempel columns of widely varying dimensions differ but slightly, it was deemed advisable to study the effects of various mechanical details. The following were given consideration: (1) Shape, size, and material of distilling bulb; (2) material of column; (3) filling material in column; (4) size of charge.

To determine the effect of the distilling bulb a series of experiments was performed in which similar Hempel columns were used in connection with different types of vessels. Comparisons were made between effects produced with glass bulbs having capacities of 500 c. c. and 300 c. c., respectively. Distillations were made from 300 c. c. bulbs with and without constrictions at the base of the fractionating column. Also a copper distilling flask was used in connection with one of the standard 6-inch columns. The results are given in the first four columns of Table 13. It appears that by using Hempel columns of approximately equal dimensions like results are obtained, whether the distilling bulb is smaller or larger, constricted or unconstricted, of glass or of copper.

The results of distillations made in an apparatus with column and bulb of copper (column 8, Table 13) differed but slightly from those obtained with a glass column.

Distillations were made, using glass instead of aluminum beads as filling material in the column; and it was learned that this factor is of little effect as far as the numerical results of an analysis are concerned. Also distillations were run with an initial charge of 100 grams of oil, and in these there was a tendency for the cuts at higher temperatures to be consistently a little low. This effect was undoubtedly caused by the lag of the distilled oil in the condenser tube.

TABLE 13.—*Results of distillations with various modifications of the Hempel apparatus.*

[Note close agreement of results, indicated especially by the small average variations.]

Flask temperature, °C.	6-inch by 1-inch column, with 5 inches of aluminum beads.			Flask of optimum dimensions.b		Slender column.c	Medium column.d	Copper column and bulb.e	Same as No. 4, but with 100-gram charge of oil.	Average of Nos. 1 to 5.	Average of Nos. 1 to 9.
	Copper bulb.	Creosote flask.a		Aluminum beads.	Glass beads.						
		Standard.	Small bulb.								
	1	2	3	4	5	6	7	8	9		
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
100	6.3	6.2	6.2	5.9	6.2	5.9	5.8	6.2	6.5	6.2	6.1
125	6.3	6.1	6.5	6.2	6.1	6.1	6.2	5.8	5.8	6.2	6.1
150	6.0	6.4	6.4	6.2	6.2	6.6	6.1	6.7	6.1	6.2	6.3
175	6.8	6.7	6.6	6.5	6.6	7.1	6.8	7.0	6.8	6.6	6.8
200	6.3	6.6	6.5	6.6	6.7	6.6	6.5	6.6	6.1	6.5	6.5
225	6.4	6.5	6.4	6.2	6.3	6.2	6.2	6.2	6.2	6.4	6.3
250	6.5	6.6	6.5	6.4	6.4	6.9	6.6	6.6	6.2	6.5	6.5
275	f[7.0]	6.1	5.9	6.2	f[6.8]	f[7.0]	6.1	6.2	6.1	6.0	6.1
Average cut										6.3	6.3
Average variation										1.6	2.3

a Flask used by Forestry Service, see figure 6.
b This flask is shown in figure 16.
c Five-eighth-inch column used in experiments shown in Table 12.
d Three-quarter-inch column used in experiments shown in Table 12.
e Column 6 inches high and 1 inch in diameter, containing 5 inches of aluminum beads.
f Bracketed results omitted from average; they include drainage of condenser at end of distillation.

Table 13, which summarizes the effects of all the types of 6-inch Hempel columns that were employed, shows that the average variation (2.3 per cent) in the amounts of the cuts is practically the same between different methods as between duplicate distillations by any one method. If comparisons are limited to cuts made with glass columns 6 inches long and 1 inch in diameter, the average variation is only 1.6 per cent. The results clearly demonstrate the fact that by using efficient fractionating columns of approximately equal dimensions most of the other factors that affect results of distillation are made negligible.

MECHANICAL ADVANTAGES OF DIFFERENT TYPES OF APPARATUS.

Without results of trial in the hands of a considerable number of operators it is difficult to draw definite conclusions regarding the mechanical advantages of the different types of apparatus, but the experiments indicate that a simple flask with an unconstricted column 1 inch in diameter and holding 5 inches of aluminum beads (see fig. 16) is most satisfactory. There seems to be little question as to the desirability of employing a fractionating column approximately of the size indicated. The details of material and method of construction are a little less definitely established, but it is believed that the flask selected approaches an optimum with regard to sim-

plicity and convenience of operation. Other types of apparatus have certain advantages and may be better adapted to special cases. For example, an apparatus consisting of a copper bulb and either a copper or a glass column has been found better in the distillation of certain cracked oils that have a tarry residue. The process of cleaning the longer necked flask is laborious and the danger of breakage so great that the two-piece apparatus seems best, and the results have been found to duplicate exactly those of the other apparatus.

A column of large rather than of small bore is desirable, as it minimizes the possibility of flooding and also reduces the danger of variations being caused by air currents and atmospheric temperature changes. Dispensing with a constriction at the base of the fractionating column also seems desirable, as it permits the use of a shorter and less unwieldy flask, facilitates cleaning the distilling vessel, and tends to lessen the danger of flooding. There are numerous simple mechanical devices by which the column of beads may be conveniently supported. One which has been used is a copper wire, shaped into a spiral at one end and with a hook at the other, which can be pushed into the outlet tube of the flask. Another device, which is more secure, consists of a circle of gauze fastened to a copper wire, which in turn is attached to a circle of spring metal that holds by expansion against the wall of the neck in the space between the outlet tube and the cork.

FIGURE 16.—Hempel column of optimum dimensions for distillation of petroleum.

Aluminum beads seem better than glass, though there was no marked difference in the efficiency attained. (See Table 13, columns 4 and 5.) Glass beads fit together more tightly and on that account are more liable to flood.

CRACKING AS A FACTOR IN ANALYTICAL DISTILLATION WITH STILL HEADS.

As has been stated in a previous page, it is desirable in making analytical distillations of petroleum to minimize, or if possible entirely eliminate, the factor of "cracking." The object of an analysis is to determine what constituents an oil contains and not

what may be made from it by cracking. The possibility of cracking, therefore, must be considered in the selection of apparatus for a standard method of analysis.

It is first necessary to understand the nature of the cracking process; and the following statements, which may be accepted as axiomatic, bring out the most important points in the present connection:

The cracking of heavy hydrocarbons by heat is to be regarded as simply an instance of the general rule that organic compounds are decomposed by heat. It is well known that the simpler petroleum hydrocarbons are stable at much higher temperatures than those of high molecular weight.[a]

It appears, therefore, that when two hydrocarbons are at the same temperature, the one that has the greatest molecular weight and consequently the higher boiling point is decomposed to the greater extent.

It is a well-established fact in the commercial art of refining petroleum that cracking may be brought about by the use of stills with efficient fractionating columns. It follows, likewise, that in the laboratory cracking is most likely to occur with apparatus giving efficient fractionation. This fact has led to a widespread distrust of still heads, which is largely due to a misconception of the mechanism of the process of cracking and to ignorance of the limits within which cracking occurs. It is commonly believed that, when vapors condense in the fractionating column and run back into the retort, they are superheated when they strike the surface of the boiling liquid, and this superheating above their normal boiling points brings about cracking. In actual fact, the mechanism of the process is totally different. The condensates are of much lower molecular weight than the liquid constituents remaining in the retort and could not be as extensively decomposed as the latter, even if, on running back, they attained the maximum temperature of the still, which is that of the boiling liquid. This they can never do, because they are in large part immediately revolatilized from the surface of the liquid, and in course of this change of state absorb "latent heat," thus producing local cooling. It appears, therefore, that the condensates can never quite attain the temperature of the boiling liquid; and if they do, they will undergo less extensive decomposition than the constituents of the latter.

The phenomenon of cracking is, therefore, to be explained on the basis of the amount of heat supplied to the liquid phase of the distilling system, and is independent of the quantity of condensate returned from the fractionating column, except as that affects the tem-

[a] Brooks, B. T., Bacon, R. F., Padgett, F. W., and Humphrey, I. W., The preparation of gasoline and kerosene from heavier hydrocarbons: Jour. Ind. and Eng. Chem., vol. 7, March, 1915, pp. 180–185.

perature necessary to force vapors over into the condenser. For a column of given dimensions and construction a certain temperature gradient is necessary, in order to drive vapors up and over into the condenser. This gradient varies with the composition of the mixture distilled and also with the temperature during any one distillation; but, all other factors being equal, it is proportional to the amount of condensation produced. Consequently, with a given oil it is necessary to have a temperature difference between the liquid phase and the vapor at the outlet, which difference is dependent upon the efficiency of the column. The more efficient the column, the hotter the liquid must be and the greater are the possibilities of cracking. The factor of cracking is also controlled by the extent and the temperature of the heated contact surface; but this effect may, for present considerations, be included in that of heating liquid above the temperature of the escaping vapor.

Hence the problem resolves itself into two parts, as follows: (1) The determination of the amount that the temperature of the liquid must exceed that of the vapor in order to bring about sufficient cracking to be evident in the percentage and specific gravity results of a distillation. This difference in temperature furnishes an index of the relative possibility of cracking characteristic of each type of apparatus; (2) the determination of the approximate temperature at which cracking begins with various types of oil.

DETERMINATION OF RELATIVE PROBABILITIES OF CRACKING IN THE HEMPEL AND OPEN-FLASK METHODS.

Determinations were made of the approximate temperatures of the liquid phase during the course of the various distillations. The recess in the copper flask, described on page 54 and shown in Plate I, was filled with paraffin and a thermometer was placed in it. It was found that with the 6-inch Hempel apparatus the liquid was about 40° C. hotter than the vapor when the temperature of the vapor reached 300° C. The difference in the case of the open-flask method was about 10°, with the same vapor temperature. It is to be noted that this difference is not characteristic of the apparatus as regards the absolute amount indicated, for it was found that the difference varied in the course of a distillation, being greater in the earlier stages when the oil was more complex. For example, the liquid was about 75° hotter than the vapor in the Hempel apparatus when the temperature of the vapor was about 50° C. It appears, however, that a distillation by the Hempel method may be carried within 25° or 30° of the limit possible for an open-flask distillation without any greater possibility of cracking than is incident to the latter.

DETERMINATION OF THE TEMPERATURE AT WHICH CRACKING BEGINS WITH VARIOUS OILS.

There are several possible methods of determining whether or not cracking occurs in the course of a distillation. Chemical tests of distillate and residue would indicate changes in the degree of saturation that are always bound to occur when petroleum is decomposed. Specific gravity measurements would indicate cracking if the suspected fractions showed apparent abnormalities with regard to this property. Likewise it is generally possible to observe when cracking occurs, as the distillation continues for some time with little or no increase in temperature and yields a distillate that generally has a characteristic dirty yellow color. Cracked distillates also have a disagreeable burnt odor, but this is noticeable when the amount of decomposition is too small to affect the percentage and specific gravity relations.

The simple scheme adopted in these experiments to procure quantitative data was to note changes in the amount of oil distilling up to a given temperature limit. The procedure was as follows: A carefully weighed charge of oil was distilled up to some given temperature, the condenser allowed to drain, and the distillate weighed. The distilling flask was allowed to cool and the distillate poured back. A redistillation was then made and stopped at the same temperature, care being taken that conditions of heating were at the end identical with those of the first distillation. The amount distilled was again determined by weighing and the process of redistillation repeated for a second and perhaps a third time. It is obvious that if no cracking occurred the percentages distilled would always be the same within the limits of experimental error. It was at first thought that if cracking occurred the amounts distilled would progressively increase with successive redistillations, but such was not the case. In cases when there were various qualitative indications of cracking, the percentages obtained on the second distillation were considerably less than those obtained from the first. After the second fractionation the percentages distilling remained approximately constant. No explanation is offered of the exact mechanism by which this result is accomplished, as the data at hand are insufficient to establish the theory which seems most probable. There is no shadow of doubt, however, as to the fact that decrease in amount distilled is a definite indication of the occurrence and approximate degree of cracking.

OILS USED IN EXPERIMENTS.

Four oils were examined with regard to the phenomenon of cracking in the course of an analytical distillation: One was the Pennsyl-

vania crude used in the general experiments described on pages 52 to 65, two were from Oklahoma, and one from California.

TEMPERATURES.

The temperatures used as upper distillation limits varied from 289° to 330° C. and were measured without applying a correction for the exposed stem of the thermometer. The actual temperatures were 10° to 20° higher.

RESULTS OF EXPERIMENTS.

The results are shown in Table 14. No cracking occurred in the Pennsylvania oil even at a temperature of 325° C., although this was undoubtedly near the limit. In other cases Pennsylvania oils were found to crack at temperatures between 310° and 320° C. With the Oklahoma oils and the California oil there was no cracking at 300° C., but this action occurred in marked degree between 300° and 325°, and in one case, at least, between 300° and 302° C. Two experiments were made in which it was attempted to distill an Oklahoma oil up to 335° C. In both experiments cracking occurred so extensively at 330° C. that it was difficult to increase the temperature of the vapor above 330°.

TABLE 14.—*Cracking temperatures of several crude oils. Measured in flask with 6-inch Hempel column.*

[Cracking indicated by marked decrease in amount distilled on second distillation.]

Oil	Pennsylvania.				Oklahoma No. 1.			Oklahoma No. 2.			California.	
Temperature (uncorrected) of vapor at end of distillation, ° C	289	312	312	325	300	a 308	a 325	300	b 330	b 330	360	325
First distillation, percentage by weight	57.0	65.0	64.8	70.1	39.9	54.3	61.5	49.7	.....	.....	49.1	66.3
Second distillation, percentage by weight	56.7	64.5	64.8	69.6	40.7	49.1	55.3	48.9	.....	.....	48.6	60.2
Third distillation, percentage by weight	58.7	66.1	65.3	70.0	41.0	48.9	56.0	49.2	.....	.....	49.3	59.9
Fourth distillation, percentage by weight	.....	66.7	66.2	.....	41.0	49.3	57.1	48.9	.....	.....	49.6	60.3
Fifth distillation, percentage by weight	.....	.....	66.3	.....	.....	.....	.....	.....	.....	.....	.....	.....
Residue, percentage by weight	42.0	33.0	32.5	28.6	58.6	49.8	42.0	49.7	.....	.....	48.5	.....
Residue plus last distillate, percentage by weight	98.7	99.7	98.8	98.6	99.6	99.1	99.1	98.6	.....	.....	98.1	.....
Loss, percentage by weight	1.3	0.3	1.2	1.4	0.4	0.9	0.9	1.4	.....	.....	1.9	.....

a Cracking indicated. Note decrease in case of second distillation.
b An attempt was made to distill to 335° C., but temperature of vapor could not be raised above 330° C., a large quantity distilling at this point without change in thermometer reading.

DISCUSSION OF RESULTS OF TESTS.

From these experiments it appears that it is possible to distill oils obtained from the three important fields of this country until

the vapor temperature reaches about 300° C. Above this temperature there is a probability of cracking, which is less with the Pennsylvania petroleum than with the other oils tested. Above 325° C. marked cracking takes place, and distillations at temperatures above 325° are unreliable in what they show concerning the original composition of an oil. In any event cracking may be readily detected through the qualitative indications of continued distillation without increase in temperature.

The general conclusion to be reached from the results of the experiments just described is that, while the possibility of cracking is slightly greater with the Hempel than with the open-flask methods, it is still of negligible importance provided that in the distillation the vapor temperature does not exceed 300° C.

GENERAL SUMMARY.

The chief points covered in this report may be summarized as follows:

1. The analytical distillation of petroleum is a process of immense importance to producers, refiners, retailers, and consumers.

2. Methods of petroleum distillation have not been standardized, and are not based on comprehensive and definite scientific knowledge, but rather on factors such as personal preference and ease of operation.

3. Frequent disputes arise on account of lack of agreement among the distillation reports of various chemists, and the failure of the reports of laboratory analyses to agree with results obtained in the refinery.

4. A series of experiments was performed for the purpose of studying the characteristics of three general types of distillation methods, involving maximum separation, moderate separation, and minimum separation, with the following results:

(a) The results of a series of primary distillations indicated certain similarities and also marked differences among the percentage-temperature and percentage-specific gravity relations discovered.

(b) A series of redistillations showed that the similarities noted were entirely superficial, and that the actual degrees of fractionation attained were widely different. The Hempel method, representative of maximum separation, attained an efficiency of 56 per cent on the arbitrary and empirical scale fixed by the nature of the experiments, the Engler-Ubbelohde method was rated at 26 per cent on the same scale, and the Allen-Jacobs at 14 per cent. Two successive Engler-Ubbelohde distillations attained a rating of 44 per cent, showing that a single Hempel distillation produced more efficient separation than two or probably three open-flask distillations.

(*c*) Concordant analytical results are more difficult to obtain by the method of moderate separation than by the method of minimum or that of maximum separation.

(*d*) The higher degree of fractionation obtained by the Hempel method indicated the desirability of the class it represents for the analytical distillation of petroleum.

5. On the basis of results indicated by the study of the three classes of distillation methods a comprehensive study was made of the efficiencies of all the types of fractionation apparatus available to the petroleum chemist, with results as follows:

(*a*) A number of stills were found to be of practically equal efficiency.

(*b*) Of these several failed to work throughout the necessary range of temperature.

(*c*) Of the three or four that worked well one, the Hempel, had marked advantages in the way of cheapness, availability, simplicity, and durability.

6. The characteristics of various forms and types of Hempel still heads were studied in detail.

(*a*) It was found that nearly identical results could be obtained with a wide range of latitude in height of column, diameter of column, nature of filling material, size of bulb, and general construction of apparatus.

(*b*) For mechanical reasons a column measuring 6 inches from bulb of flask to outlet tube and 1 inch in diameter was found most satisfactory.

(*c*) For general use a certain apparatus, of which the dimensions and general appearance are shown in figure 16, seemed most desirable. The column and the bulb were made of glass and of one piece with no constriction at the base of the neck. For special types of distillation work, apparatus of different construction may be employed advantageously and without affecting the accuracy of the results.

7. Cracking was shown by experimental evidence of two sorts to be a factor of no importance as an objection to the use of efficient still heads in the distillation analysis of petroleum.

PUBLICATIONS ON PETROLEUM TECHNOLOGY.

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INDEX.

77